

**DETERMINATION OF
ORGANOCHLORINE COMPOUNDS IN WATER
USING MICRO-SCALE EXTRACTION**

RAC Project No. PDF12

MINISTRY OF ENVIRONMENT AND ENERGY

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Report prepared by:

Iris D. Albrecht

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Abstract

This report describes the study of hexane micro-liquid-liquid extraction, and the preliminary work using solid phase micro-extraction (SPME) for the analysis of organochlorine pesticides (OCs), chlorinated benzenes (CBs) and polychlorinated biphenyls (PCBs) in water.

The hexane micro-liquid-liquid extraction procedure consists of a single-step 60-90 minute extraction of 800 mL water with 2 mL n-hexane, followed by gas chromatographic (GC) analysis of the compounds in the hexane layer. Several aspects of the procedure were investigated, including extraction efficiency, speed, accuracy and precision.

The method performance was compared to that of the currently used Ontario Ministry of Environment and Energy method OWOC-E3120B. Hexane micro-extraction gave equivalent or superior recoveries of OCs and CBs spiked in reagent water, with a higher degree of precision. Method detection limits were determined from repetitive low level spiking experiments for all but two compounds, and were either at or below the current specifications set by the Ontario Ministry of the Environment and Energy. To monitor matrix effects on the method, OCs and CBs were spiked in raw and treated water samples. Also in these cases the recoveries obtained with hexane micro-extraction either matched or surpassed those obtained by method OWOC-E3120B.

The performance of hexane micro-liquid-liquid extraction was tested on groundwater samples known to be contaminated with PCBs and CBs. The method was compared against method OWOC-E3120B using statistical analysis of paired observations. For OCs hexane micro-extraction performed adequately, consistently yielding greater than 90% recoveries relative to the current method. In contrast, the recoveries of PCBs with hexane micro-extraction was poor and highly variable. To solve this problem, extraction efficiencies can be enhanced

by increasing the solvent-to-water ratio. Detection limits and/or increased manipulation steps might limit this option.

Solid phase micro-extraction is a solventless single-step extraction procedure, based on the partitioning of compounds between the aqueous phase and a polymeric stationary phase, which is coated on a small diameter silica fibre. The coated fibre makes up part of a modified GC syringe, and is placed into the injector of a gas chromatograph, where the extracted compounds are thermally desorbed and analyzed.

Experimentation with this method involved optimization of extraction and desorption conditions using spiked water samples containing a mixture of half the target OC and CB compounds. Generally, very impressive recoveries were indicated, especially of the less volatile compounds. However, one of the difficulties encountered was the carry-over of Mirex between injections, presumed due to sorption on active sites of the glass fibre surface. Fibre deactivation prior to coating will likely solve this problem.

Long equilibration times were indicated by the less volatile compounds, which might put into question the efficiency of the method compared to hexane micro-liquid-liquid extraction, from the standpoint of sample throughput. Equilibration and desorption times should be reassessed using deactivated glass surfaces on the fibre and sample vials. Solid phase micro-extraction is an attractive method for its simplicity and detection capabilities, but more work is needed to assess its viability as a replacement method for the OWOC-E3120B.

Hexane micro-liquid-liquid extraction is also a fast and convenient procedure. In this study this method was shown to be capable of precise and accurate measurements for organochlorine pesticides and chlorinated benzenes in water, but more work is needed to include the analysis of PCBs and Toxaphene.

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The diligent work of Jadwiga Mazur was instrumental in the success of this project, particularly in the studies pertaining to the comparison of hexane micro-extraction to the current method of analysis.

Table of Contents

Abstract.....	i
Acknowledgement.....	iii
List of Tables.....	ix
List of Illustrations.....	xi
1. Background and objectives.....	1
1.1. Introduction.....	1
1.2. Analysis of organochlorine pesticides, polychlorinated biphenyls, and other chlorinated organic compounds in water.....	2
1.3. Theory of liquid-liquid extractions.....	5
1.3.1. Micro liquid-liquid extraction.....	6
1.3.2. Solid phase micro-extraction.....	7
1.4. Project Objectives.....	8
1.4.1. Hexane micro-extraction.....	8
1.4.2. Solid phase micro-extraction.....	9
2. Materials and methods.....	11
2.1 Glassware, equipment and chemicals.....	11
2.2. Preparation of intermediate, spiking and calibration standards.....	13
2.2.1. Preparation of intermediate solutions....	13
2.2.1.1. Intermediate solution of 1,3,5- Tribromobenzene.....	13
2.2.1.2. Intermediate solution of OC/CB "A" compounds.....	13
2.2.1.3. Intermediate solution of OC/CB "B" compounds.....	15
2.2.2. Preparation of spiking solutions.....	16
2.2.3. Preparation of instrument calibration solutions.....	18
2.3. Extraction procedures and sample preparation....	20
2.3.1. Hexane micro-extraction.....	20
2.3.1.1. Recoveries of spiked compounds.....	20
2.3.1.2. Extraction of Smithville samples....	21
2.3.1.3. Experimental variations.....	21
2.3.2. Solid phase micro-extraction.....	22
2.4. Instrumental analysis.....	27
2.4.1. Equipment.....	27
2.4.2. Instrument parameters.....	27
2.4.2.1. Gas supply.....	27
2.4.2.2. Basic GC parameters.....	27
2.4.2.3. Details of GC configuration inputs...	28
2.4.3. Data aquisition and manipulation using Chrom Perfect™.....	30

2.4.4.	Sample chromatograms and report printouts for OC/CB compounds.....	31
3.	Preliminaries.....	37
3.1.	General comments.....	37
3.2.	Instrument performance.....	37
3.2.1.	Linearity.....	37
3.2.2.	Within-run instrument precision.....	40
3.3.	Extraction parameters.....	42
3.3.1.	Volume of hexane required.....	42
3.3.2.	Time required for extraction.....	45
3.3.3.	The use of 1,3,5-Tribromobenzene as internal/surrogate standard.....	46
3.4.	Extraction efficiency.....	48
3.5.	Summary.....	49
4.	Hexane micro-extraction of spiked reagent water.....	51
4.1.	General comments.....	51
4.2.	Analyte recovery.....	53
4.3.	Comparison of recoveries: Hexane micro- extraction versus method OWOC-E3120B.....	55
4.4.	Determination of MDLs, "W" and "T" values.....	59
4.4.1.	MDLs for OC/CB "A" compounds.....	59
4.4.2.	MDLs for OC/CB "B" compounds.....	62
4.4.3.	MDL determination for PCBs.....	62
4.5.	Summary.....	65
5.	Hexane micro-extraction of spiked real waters.....	67
5.1.	General comments.....	67
5.2.	Recovery from real water samples.....	68
5.3.	Comparison of extraction methods.....	72
5.4.	Summary.....	78
6.	Hexane micro-extraction of groundwater samples contaminated with PCBs and chlorinated benzenes.....	79
6.1.	General comments.....	79
6.2.	Comparison by sample population means.....	79
6.3.	Comparison by paired observations.....	81
6.4.	Salting samples.....	86
6.5.	Summary.....	86
7.	Preliminary experimentation with solid phase micro-extraction (SPME).....	89
7.1.	General comments.....	89

7.2.	Fibre preconditioning.....	89
7.3.	SPME of HPLC water and HPLC water spiked with OC/CB "A" compounds.....	90
7.3.1.	Sample preparation, extraction and instrument conditions.....	90
7.3.2.	Results.....	92
7.4.	Optimization of injection temperature and desorption time.....	96
7.5.	Equilibration time.....	101
7.6.	Summary.....	101
8.	Conclusions and Recommendations.....	105
8.1.	Hexane micro-liquid-liquid extraction.....	105
8.2.	Solid phase micro-extraction.....	107
9.	References.....	111
Appendix 1:	Detector response vs concentration for OC/CB "A" compounds.....	115
Appendix 2:	Replicate spike recoveries for the determination of MDLs, "W" and "T" values.....	125
Appendix 3:	Comparing methods: Replicate spike recoveries from reagent and Verner raw water using hexane micro-extraction and method OWOC-E3120B.....	153
Appendix 4:	Interpretation of data from a study investigating the stability of Trifluralin in solution.....	175

List of Tables

Table 2.1:	Stock solutions used for this project.....	12
Table 2.2:	Intermediate solution OCA-NOV15-INT.....	14
Table 2.3:	Intermediate solution OCB-NOV15-INT.....	15
Table 2.4:	Preparation of spiking solutions.....	16
Table 2.5:	Preparation of instrument calibration solutions.....	19
Table 2.6:	Experimental parameters for hexane micro- extractions.....	23
Table 3.1:	Concentration ranges of OC/CB "A" components for the determination of instrument linearity....	38
Table 3.2:	Linear dynamic range for OC/CB "A" compounds...	40
Table 3.3:	Instrument precision.....	41
Table 3.4:	Percent recoveries of OC/CB "A" compounds in reagent water extracted with 1, 2, or 3 mLs hexane.....	44
Table 3.5:	Results of ANOVA evaluation of effect of hexane volume.....	45
Table 3.6:	Confidence intervals of percent recoveries....	48
Table 3.7:	Measured extraction efficiency of the hexane micro-extraction method.....	50
Table 4.1:	Percent recovery for various sets of experiments of hexane micro-extraction of reagent water spiked with OC/CB "A" compounds.....	52
Table 4.2:	Percent recovery for various sets of experiments of hexane micro-extraction of reagent water spiked with OC/CB "B" compounds.....	52
Table 4.3:	Percent recoveries of Trifluralin, PCBs and Toxaphene.....	55
Table 4.4:	Comparison of recoveries obtained by method OWOC-E3120B and hexane micro-extraction: HPLC water spiked with OC/CB "A" compounds.....	56
Table 4.5:	Comparison of recoveries obtained by method OWOC-E3120B and hexane micro-extraction: HPLC water spiked with OC/CB "B" compounds.....	57
Table 4.6:	MDLs, "W" and "T" values of OC/CB "A" compounds.....	60
Table 4.7:	MDLs, "W" and "T" values of OC/CB "B" compounds.....	63
Table 5.1:	Percent recovery by hexane micro-extraction of compounds OC/CB "A" spiked in real water samples, compared to reagent water spikes.....	69
Table 5.2:	Percent recovery by hexane micro-extraction of compounds OC/CB "A" spiked in real water samples, compared to reagent water spikes.....	70

Table 5.3:	Comparison of extraction methods: Recoveries of OC/CB "A" compounds from Verner raw water.....	73
Table 5.4:	Comparison of extraction methods: Recoveries of OC/CB "B" compounds from Verner raw water.....	74
Table 6.1:	Comparison of method OWOC-E3120B and hexane micro-extraction methods with real samples.....	80
Table 6.2:	Paired determinations of 1,2,4-TCB resulting from method OWOC-E3120B and hexane micro- extraction.....	82
Table 6.3:	Paired determinations of 1,2,3-TCB resulting from method OWOC-E3120B and hexane micro- extraction.....	83
Table 6.4:	Paired determinations of 1,2,3,4-TCB resulting from method OWOC-E3120B and hexane micro- extraction.....	84
Table 6.5:	Paired determinations of PCBs resulting from method OWOC-E3120B and hexane micro- extraction.....	85
Table 6.6:	Paired determinations of PCBs resulting from method OWOC-E3120B and hexane micro- extraction of salted samples.....	87
Table 7.1:	Comparison of peak area count in the chromatograms of OCAINST-MAR30 and SPME of spiked HPLC water.....	95
Table 7.2:	Desorption conditions and measured percent residual compounds carried over.....	100

List of Illustrations

Figure 2.1:	Channel 1 (DB-1) output of instrument calibration standard OC/CB "A".....	32
Figure 2.2:	Channel 2 (DB-1701) output of instrument calibration standard OC/CB "A".....	33
Figure 2.3:	Channel 1 (DB-1) output of instrument calibration standard OC/CB "B".....	34
Figure 2.4:	Channel 2 (DB-1701) output of instrument calibration standard OC/CB "B".....	35
Figure 3.1:	Detector response versus concentration for OC/CB "A" compounds.....	39
Figure 3.2:	Area counts versus time of extraction for OC/CB "A" compounds.....	47
Figure 5.1:	Compounds with poor recoveries from Verner raw water.....	71
Figure 5.2:	Examples of improved recoveries by hexane micro-extraction.....	75
Figure 5.3:	Comparisons of chlorinated benzene recoveries by both methods.....	76
Figure 5.4:	Comparison of recoveries for late eluting compounds.....	77
Figure 7.1:	Fibre blank run after preconditioning a fibre coated with 7 μ m polydimethylsiloxane..	91
Figure 7.2:	Channel 1 (DB-1) chromatograms of OCAINST -MAR30 and SPME of spiked HPLC water.....	93
Figure 7.3:	Channel 2 (DB-1701) chromatograms of OCAINST -Mar30 and SPME of spiked HPLC water.....	94
Figure 7.4:	Superimposed chromatograms of SPME water blank and SPME of water spiked with OC/CB "A" compounds.....	97
Figure 7.5:	DB-1 column chromatograms of SPME of water spiked with OC/CB "A" compounds, and residual compounds on the fibre.....	98
Figure 7.6:	DB-1701 column chromatograms of SPME of water spiked with OC/CB "A" compounds, and residual compounds on the fibre.....	99
Figure 7.7:	SPME time profiles of OC/CB "A" compounds: peak area versus time of extraction.....	102

1. Background and objectives

1.1. Introduction

Analytical chemists have been under increasing pressure to find ways of lowering method detection limits in order to monitor trace levels of contaminants in the environment. While monumental improvements in instrumentation and instrumental detection limits have developed over the years, there has been a growing emphasis on improving the efficiency and reliability of the front end of the analytical scheme, namely the sampling and sample preparation methods¹. This is of fundamental importance, since errors introduced before the actual analysis cannot be compensated for by even the most advanced methods of instrumentation. Clearly, no matter how often a given instrumental analysis is repeated and how sensitive and precise it may be, the final analysis will still yield results that are grossly unrepresentative of the system of interest if inappropriate sampling and/or sample handling has occurred¹⁻³. This problem is particularly relevant in environmental analysis.

When considering laboratory procedures, the analytical process normally begins with sample preparation². This includes removal of the analytes from the matrix via an extraction procedure (analyte isolation), removal of interfering compounds from the extract (clean up), and concentration of the extract to the required levels for instrumental detection (analyte enrichment). Although considerable improvements in analyte isolation and enrichment methods have evolved over the years, including solid phase extraction⁴⁻⁶, supercritical fluid extraction^{7,8}, liquid-liquid micro-extraction⁹⁻¹³ and

solid phase micro-extraction¹⁴⁻²¹, many current sample preparation procedures are based on old methods, which require large quantities of organic solvents^{1,5,22}.

One such method, which continues to be the most common method of extraction for the determination of semi-volatile organic compounds in water is liquid-liquid extraction²². However, the use of large quantities of solvent is in principle undesirable. Considerations of laboratory safety, operating cost, and efficiency (as measured by sample throughput), has recently provided an enormous incentive to reduce the use of organic solvents in analytical laboratories, and consequently, has increased the need to develop alternative extraction methods.

As part of these efforts this project (PDF12) was initiated to establish a method using micro-extraction procedures as a means of improving the existing MOEE method OWOC-E3120B, for the determination of organochlorine pesticides (OCs), polychlorinated biphenyls (PCBs) and other chlorinated organic compounds in water samples^{23,24}.

1.2. Analysis of organochlorine pesticides, polychlorinated biphenyls and other chlorinated organic compounds in water.

The current MOEE method for the determination of OCs, PCBs and other chlorinated organic compounds in water samples specifies liquid-liquid extraction using dichloromethane as solvent²³. This is a very labour intensive procedure, requiring three serial extractions, drying over sodium sulfate, volume reduction via rotodistillation, clean-up by open column liquid chromatography, and a second volume reduction procedure. Aside from concerns of increased risk to the analyst from exposure to large volumes of chlorinated solvent, there are four other major factors which make this procedure undesirable:

- (1) **Cost of solvent and disposal:** In order to avoid sample contamination and false positive determination, expensive high purity solvents are required. After use, the spent solvent must be properly disposed of, thereby adding to the cost of analysis.
- (2) **Sample throughput:** This method is very time consuming. One set of samples takes two days to prepare for instrumental analysis.
- (3) **Personnel requirement:** This is a laborious method that is not amenable to automation. During peak seasons additional personnel are sometimes employed to keep up with the workload.
- (4) **Accuracy:** The multitude of sample manipulation steps in this procedure provide many opportunities for analyte losses to occur.

The desire to minimize costs of solvent use and disposal, decrease sample preparation time, and minimize interferences contributed by the solvent itself has resulted in the development of micro-liquid-liquid extraction methods. Examples include USEPA methods 504 and 505 both of which use 2 mL of hexane to extract analytes from 35 mL water samples, and USEPA method 551 which uses 2 mL of methyltertbutyl ether to extract chlorinated solvents and other compounds from 35 mL water samples²². Haloacetic acids and chlorophenols have been micro-extracted from 30 mL water samples with 2 mL methyltertbutyl ether¹¹, and organophosphorus pesticides have been successfully micro-extracted from water with hexane¹².

Considering this project's objectives from the standpoint of analyte type, USEPA method 505 is particularly relevant, since the method targets many of the analytes specified by MOEE method OWOC-E3120B^{10,23}, and therefore provides strong evidence that micro-liquid-liquid extraction using hexane might be a viable alternative to the extraction

procedure currently described in method OWOC-E3120B. Extension of method 505 to the analysis all of the organochlorine compounds targeted in method OWOC-E3120B, with some modifications in order to meet the detection limits set by the MOEE, would be the only major steps needed in order to establish validity of the method for MOEE applications.

Another more recent approach to sample extraction and preparation, that completely eliminates the use of organic solvent, is solid phase micro-extraction (SPME), developed by J. Pawliszyn at the University of Waterloo¹⁴⁻²¹. This is a non-exhaustive extraction method, and is based on the partitioning of analytes between a liquid or gaseous sample into a polymeric stationary phase, which is coated on a small diameter silica fibre. The coated fibre itself makes up part of a modified GC microsyringe. After equilibration with the sample, the fibre is placed into the injector of a gas chromatograph where the analytes are thermally desorbed, focused onto the GC column, and subsequently analyzed.

This method has shown promise for the analysis of a wide variety of compounds in water, including benzene, toluene, ethyl benzene and xylene isomers¹⁵⁻¹⁸, polyaromatic hydrocarbons^{18,21}, methyl, nitro and chloro substituted phenols^{19,20} and polychlorinated biphenyls²¹.

One of the more recent research projects at the University of Waterloo was to demonstrate the applicability of this method to the analysis of various pesticides in water, including organochlorine pesticides²⁵. This provided the impetus to include consideration of SPME in project PDF12 as another potential alternative to the liquid-liquid extraction procedures currently used in method OWOC-E3120B.

1.3. Theory of liquid-liquid extraction

Liquid-liquid extraction (LLE) has been used for many years as an analyte isolation method in schemes for the analysis of organic compounds from environmental water samples. The method consists of extraction of the desired analytes from the sample by an organic solvent. The extraction is carried out by mixing water and an immiscible solvent followed by separation of the layers. The organic solvent is chosen on the basis of its ability to efficiently extract the desired solutes from water, its low solubility in water and low volatility, since a relatively low boiling point provides ease of evaporation during concentration steps.

After a single extraction step the ratio of the concentration of the solute, S in each phase is defined as the distribution coefficient K_D :

$$K_D = \frac{[S]_{\text{organic}}}{[S]_{\text{water}}}$$

The extraction efficiency, f , represents the fraction of the analyte in the organic phase after extraction:

$$f = \frac{n_{S,\text{organic}}}{n_{S,\text{total}}}; \quad (n = \# \text{ moles})$$

By substitution with concentration terms one obtains the following expression for extraction efficiency in terms of distribution coefficients and phase volumes:

$$f = \frac{1}{1 + \frac{V_{\text{organic}}}{K_D V_{\text{water}}}}$$

These equations form the basis for calculating values of the extraction efficiency and the partition coefficient from experimental data. The amount of analyte in each phase can be determined giving f ; then K_D can be calculated. The last equation indicates that the extraction efficiency increases as the distribution coefficient increases, whereas the extraction efficiency decreases as the volumetric ratio of water to organic solvent increases.

As an effort to achieve quantitative recovery of the analytes, LLE is usually carried out by multiple serial extractions, in which the successive organic extracts are combined into one. This results in the accumulation of a large sample extract volume, which must be concentrated. A consequence of the entire procedure is possible loss of analytes during manipulation steps, loss of the more volatile analytes in the concentration steps, and the possibility of sample contamination from the solvent.

1.3.1. Micro-liquid-liquid extraction

As indicated from the discussion above, a compromise exists between maximizing analyte recovery and imposing deficiencies in method detection limits from solvent background interferences and analyte losses during sample manipulation steps. This justifies the use of a single step non-exhaustive micro-liquid-liquid extraction method⁹ in which the water sample is extracted with a minimal amount of solvent (a few millilitres), which is then transferred to a vial, sampled with a microsyringe and analyzed by gas chromatography without further manipulation. The procedure is simple and fast, and minimizes interferences from solvent contamination, and analyte losses from manipulation steps. Several variations of this method have been used for a variety of compounds, in which the volumetric ratios of water to organic phase ranged from 5 to 4900⁹⁻¹³.

1.3.2. Solid phase micro-extraction (SPME)

The theoretical aspects of SPME are treated as liquid-liquid extractions whereby the polymeric coating of the fibre is considered as the organic liquid phase. Sensitivity can be adjusted through the fibre coating thickness, which effectively alters the water to organic phase ratio. Selectivity can be adjusted through the type of polymer coating, which effectively alters the distribution coefficient¹⁴. An assortment of fibres are now commercially available^{17,18}.

Although this is a non-exhaustive extraction, the amount of analyte recovered is concentration dependent and therefore the method is suitable for quantitative measurements^{14,15}. Calibration is achieved via standard solutions of known concentration which are extracted and analyzed under identical conditions as real samples.

The solventless nature of this technique provides benefits beyond those of the aforementioned safety and cost issues; improvements in accuracy are realized because there is no manipulation of the sample extract other than direct desorption from the fibre into the gas chromatograph injector. Furthermore, improvements in sensitivity are also achieved, since all analytes isolated from a given sample are introduced to the gas chromatograph. In contrast, with conventional solvent extraction methods a 1-2 μL aliquot of the 1-2 mL sample extract is introduced into the instrument, representing only a small fraction of the analytes originally isolated from the sample matrix.

Another attractive feature of SPME is its amenability for automation. The extraction apparatus is a modified GC syringe, which is subsequently used to introduce extracted analytes to the gas chromatograph for analysis. Recent hardware and software developments to modify and expand on the basic autosampler capabilities have yielded automatic SPME sample preparation and injection stations¹⁶.

1.4. Project objectives

The overall objective of this project was to establish a method employing a micro-extraction technique for the analysis of all the organochlorine pesticides, polychlorinated biphenyls and other chlorinated compounds specified by method OWOC-E3120B. The micro-extraction method was to be validated and brought on-line as a replacement to method OWOC-E3120B.

The emphasis was primarily on hexane micro-extraction (i.e. micro-liquid-liquid extraction with hexane), based on USEPA method 505. This method was favored over SPME because as a replacement to method OWOC-E3120B it was expected to create minimal impact on the existing laboratory protocol, while providing a significant reduction in solvent use and improvement in sample throughput. However, exploratory work on SPME was also included in the research schedule, to evaluate its possible future application in MOEE methods.

1.4.1. Hexane micro-extraction

The objective of establishing a hexane micro-extraction procedure for organichlorine pesticides, polychlorinated biphenyls and other chlorinated organic compounds in water was divided into three major tasks:

(1) Recovery of analytes spiked in reagent water:

Samples consisting of distilled deionized water spiked with known quantities of the compounds of interest were used to optimize extraction conditions, including volume of hexane required, time of extraction, and changing from the currently used external standard method of quantitation, to internal standard calculation, with the surrogate standard 1,3,5-tribromobenzene assigned as the internal standard.

Once the extraction conditions were established, several

replicate recovery studies were performed to confirm the viability of the proposed method. Concurrent extractions using method OWOC-E3120B were performed for purposes of overall comparison. Low level spiked solutions were prepared and extracted to determine method detection limits (MDLs), "W" and "T" values.

(2) Recovery of analytes spiked in real waters:

Samples of treated and raw water obtained from Verner and Lakeview water treatment plants were spiked with known quantities of the compounds of interest and extracted by hexane micro-extraction to evaluate the consequences of sample matrix effects on the proposed micro-extraction technique. Concurrent extractions using method OWOC-E3120B were also performed for purposes of comparison.

(3) Analysis of contaminated samples:

As the final step in validation of the proposed hexane micro-extraction procedure, samples known to be contaminated with PCBs and chlorinated benzenes were collected from monitoring wells in Smithville. Analyses by hexane micro-extraction were compared to those by method OWOC-E3120B.

1.4.2. Solid phase micro-extraction (SPME)

Due to time constraints only a few preliminary experiments with SPME could be scheduled. The major objective was to determine the optimal extraction and instrument parameters for recoveries of analytes spiked in distilled deionized water.

2. Materials and methods

2.1. Glassware, equipment and chemicals

Labware required for the hexane micro-extraction procedures consisted primarily of 1 litre narrow mouth amber glass bottles with teflon lined screw caps, 100 or 50 mL volumetric flasks, volumetric pipettes and disposable pasteur pipettes. The extraction equipment was a roller (80 rpm, Hotpack Corp).

Acetone (reagent grade), Hexane (distilled in glass) and Water (HPLC grade) were purchased from Caledon Laboratories, Ltd. Distilled water was produced in-house and deionized with a NANOpure™ cartridge system (SYBRON/Barnstead company).

Raw and treated water samples were obtained from the Lakeview and Verner water treatment facilities of the Ontario Clean Water Agency (OWCA). Groundwater samples containing chlorinated benzenes and PCBs were obtained from monitoring wells at a contaminated site in Smithville, Ontario.

Stock solutions (100 µg/mL in isooctane) of the target compounds studied were prepared previously by MOEE personnel according to method OWOC-E3120B. All stock solutions were kept in sealed glass ampules at a maximum temperature of 5°C. The log numbers of the stock solutions used in this project are listed in Table 2.1. Intermediate solutions of Trifluralin (#133, 5µg/mL), Toxaphene (#134, 1µg/mL), PCB (#48, 10µg/mL Aroclor™ 1254 and #49, 10 µg/mL Aroclor™ 1260), and OC/CB "A" (#146) were all previously prepared by MOEE personnel.

Sample analyses were carried out by gas-chromatography with split-splitless injection and dual ECD detection, using a Varian 3400 Gas chromatograph equipped with a model 8100

autosampler, and interfaced to a chromatography data station (Chrom Perfect™, Justice Innovations, Inc.) Details of instrumental and method parameters are given in section 2.4.

Table 2.1: *Stock solutions used for this project*

Compound (100 µL/mL in isooctane)	Log number
Hexachloroethane	S140
1,2,4-Trichlorobenzene	S166
1,2,3-Trichlorobenzene	S203, S205
2,3,6-Trichlorotoluene	S239
2,6,α-Trichlorotoluene	S255, S257
1,2,3,5-Tetrachlorobenzene	S169
Pentachlorobenzene	S263
Heptachlor	S270
α-BHC	S282
β-BHC	S285
α-Chlordane	S331
γ-Chlordane	S341
oxychlordane	S338
o,p'-DDT	S283
Methoxychlor	S290
Dieldrin	S319
Endosulfan II	S313
Mirex	S278, S280
1,3,5-Trichlorobenzene	S232
1,3,5-Tribromobenzene	S312
Hexachlorobutadiene	S237

Table 2.1 (continued)

2,4,5-Trichlorotoluene	S250
1,2,4,5-Tetrachlorobenzene	S253
1,2,3,4-Tetrachlorobenzene	S260
Hexachlorocyclopentadiene	S328
Hexachlorobenzene	S267
Aldrin	S273
p,p'-DDE	S277
Lindane	S296
p,p'-DDD	S299
p,p'-DDT	S302
Heptachlor epoxide	S422
Endosulfan I	S309
Endrin	S244
Endosulfan cyclic sulfate	S316
Octachlorostyrene	S326

2.2. Preparation of intermediate, spiking, and calibration standards

2.2.1. Preparation of Intermediate solutions

2.2.1.1. Intermediate solution of 1,3,5-Tribromobenzene (135TBB-NOV15-INT)

A solution of 100 ng/mL 1,3,5-Tribromobenzene in hexane was prepared by diluting 10 mL of stock solution (code S312) to a final volume of 100 mL.

2.2.1.2. Intermediate solution of OC/CB "A" compounds (OCA-NOV15-INT)

The OC/CB compounds were grouped into two sets as described in method OWOC-E3120B to avoid problems with chro-

matographic resolution.

A solution containing 1 to 5 $\mu\text{g/mL}$ of the OC/CB "A" target compounds was prepared from the stock solutions listed in Table 2.1. Table 2.2 lists the volumes of each individual stock solution, which were transferred with volumetric pipettes into a common 100 mL volumetric flask and diluted to the mark with hexane.

Table 2.2: *Intermediate solution OCA-NOV15-INT*

Compound name and abbreviation	Volume of stock (mL)	Final conc. ($\mu\text{g/mL}$)
Hexachloroethane (HCE)	1	1
1,2,4-Trichlorobenzene (124-TCB)	5	5
1,2,3-Trichlorobenzene (123-TCB)	5	5
2,3,6-Trichlorotoluene (236-TCT)	5	5
2,6, α -Trichlorotoluene (26 α -TCT)	5	5
1,2,3,5-Tetrachlorobenzene (1235-TCB)	1	1
Pentachlorobenzene (Penta)	1	1
Heptachlor	1	1
α -BHC	1	1
β -BHC	1	1
α -Chlordane (α -Chlordan)	2	2
γ -Chlordane (γ -Chlordan)	2	2
oxychlordane (Oxychlor)	2	2
o,p'-DDT	5	5
Methoxychlor (Methoxy)	5	5
Dieldrin	2	2
Endosulfan II (Thiodan-2)	4	4
Mirex	5	5

2.2.1.3. Intermediate solution of OC/CB "B" compounds (OCB-NOV15-INT)

A solution containing 1 to 5 µg/mL of the OC/CB "B" target compounds were prepared from the stock solutions listed in Table 2.1. Table 2.3 lists the volumes taken of each of the stock solutions, which were transferred with volumetric pipettes into a common 100 mL volumetric flask and diluted to the mark with hexane.

Table 2.3: *Intermediate solution OCB-NOV15-INT*

Compound name and abbreviation	Volume of stock (mL)	Final conc. (µg/mL)
1,3,5-Trichlorobenzene (135-TCB)	5	5
Hexachlorobutadiene (HCBD)	1	1
2,4,5-Trichlorotoluene (245-TCT)	5	5
1,2,4,5-Tetrachlorobenzene (1245-TCB)	1	1
1,2,3,4-Tetrachlorobenzene (1234-TCB)	1	1
Hexachlorocyclopentadiene (Cyclopent)	2	2
Hexachlorobenzene (HCB)	1	1
Aldrin	1	1
p,p'-DDE	5	5
Lindane	1	1
p,p'-DDD	5	5
p,p'-DDT	5	5
Heptachlor epoxide (Heptoxide)	1	1
Endosulfan I (Thiodan-1)	2	2
Endrin	4	4
Endosulfan cyclic sulfate (Thio-SS)	4	4
Octachlorostyrene (Octa)	1	1

2.2.2. Preparation of spiking solutions

The intermediate solutions described in sections 2.1 and 2.2.1 were subsequently used to prepare spiking solutions for recovery studies. Details are given in Table 2.4. All spiking solutions were diluted with Acetone to a final volume of 100 or 50 mLs. They are coded to indicate composition, type of solution, concentration relative to the spiking solution described in method OWOC-E3120B, and date of preparation. For example, OCASPKx0.5-NOV15 is a spiking solution consisting of OC "A" compounds at half the concentrations specified by method OWOC-E3120B. The internal/surrogate standard solutions of 1,3,5-Tribromobenzene indicate the date of preparation and solution concentration.

Table 2.4: Preparation of spiking solutions
(Diluted to 100 mL with acetone)

Code	Date	Solution and volume used	
Internal/surrogate standard:			
135TBB-DEC15-50ng/mL	15/12/93	135TBB-NOV15-INT	0.5mL
135TBB-FEB10-100ng/mL	10/2/94	135TBB-NOV15-INT	1mL
135TBB-MAR29-100ng/mL	29/3/94	135TBB-NOV15-INT	1mL
135TBB-MAY26-100ng/mL	26/5/94	135TBB-NOV15-INT	1mL
135TBB-JULY21-100ng/mL	21/7/94	135TBB-NOV15-INT	1mL
OC/CB "A":			
OCASPK-NOV15	15/11/93	OCA-NOV15-INT	2mL
		135TBB-NOV15-INT	1mL
OCASPK-noIS-NOV15	15/11/93	OCA-NOV15-INT	2mL
OCASPKx0.5-NOV15	15/11/93	OCA-NOV15-INT	1mL
		135TBB-NOV15-INT	1mL
OCASPKx0.3-NOV15	15/11/93	OCASPK-noIS-NOV15	30mL
		135TBB-NOV15-INT	1mL

Table 2.4 (Continued)

OCASPKx0.1-NOV15	15/11/93	OCASPK-noIS-NOV15 135TBB-NOV15-INT	10mL 1mL
OCASPKx0.1-noIS-NOV15	15/11/93	OCASPK-noIS-NOV15	10mL
OCASPKx0.04-NOV15	15/11/93	OCASPKx0.1-noIS-NOV15 135TBB-NOV15-INT	40mL 1mL
OCASPKx0.02-NOV15	15/11/93	OCASPKx0.1-noIS-NOV15 135TBB-NOV15-INT	20mL 1mL
OCASPKx0.01-NOV15	15/11/93	OCASPKx0.1-noIS-NOV15 135TBB-NOV15-INT	10mL 1mL
OCASPKx0.2-FEB1	1/2/94	OCASPKx0.1-noIS-NOV15	20mL
OCASPKx0.04-MAR12 ^A	12/3/94	OCA-NOV15-INT	0.4mL
OCASPKx0.02-MAR14	14/3/94	OCASPK-noIS-NOV15	2mL
OCASPKx0.04-MAR14 ^A	14/3/94	OCASPK-noIS-NOV15	2mL
OCASPKx0.06-MAR14 ^A	14/3/94	OCASPK-noIS-NOV15	3mL
OCASPK-MAR30 ^A	30/3/94	Solution #146	1mL
OCASPK-MAY26 ^A	26/5/94	Solution #146	1mL
OCASPKx0.8-MAY26 ^A	26/5/94	OCA-NOV15-INT	0.8mL
OCASPKx0.4-MAY26	26/5/94	OCA-NOV15-INT	0.8mL
OCASPKx0.2-MAY26	26/5/94	OCA-NOV15-INT	0.4mL
OCASPKx0.1-MAY26	26/5/94	OCA-NOV15-INT	0.2mL
OCASPKx0.08-MAY26 ^A	26/5/94	OCASPKx0.8-MAY26	5mL
OCASPKx0.04-MAY26 ^A	26/5/94	OCASPKx0.4-MAY26	5mL
OC/CB "B":			
OCBSPK-DEC15	15/12/93	OCB-NOV15-INT	2mL
OCBSPKx0.2-FEB1	1/2/94	OCBSPK-DEC15	20mL
OCBSPKx0.04-MAR22	22/3/94	OCBSPK-DEC15	4mL
OCBSPKx0.08-MAR22	22/3/94	OCBSPK-DEC15	8mL
OCBSPKx0.12-MAR22	22/3/94	OCBSPK-DEC15	12mL
OCBSPKx0.4-MAR22	22/3/94	OCB-NOV15-INT	0.8mL
OCBSPKx0.8-MAR22 ^A	22/3/94	OCB-NOV15-INT	0.8mL
OCBSPK-MAR22	22/3/94	OCB-NOV15-INT	2mL
OCBSPKx0.04-MAY3	3/5/94	Prepared by J. Mazur	

Table 2.4 (Continued)

OCBSPKx0.08-MAY3	3/5/94	Prepared by J. Mazur	
OCBSPKx0.8-MAY3	3/5/94	Prepared by J. Mazur	
OCBSPKx0.12-MAY3	3/5/94	Prepared by J. Mazur	
OCBSPK-MAY26 ^A	26/5/94	OCB-NOV15-INT	1mL
		135TBB-NOV15-INT	0.5mL
OCBSPKx0.8-MAY26 ^A	26/5/94	OCB-NOV15-INT	0.8mL
OCBSPKx0.4-MAY26	26/5/94	OCB-NOV15-INT	0.8mL
OCBSPKx0.2-MAY26	26/5/94	OCB-NOV15-INT	0.4mL
OCBSPKx0.1-MAY26	26/5/94	OCB-NOV15-INT	0.2mL
Trifluralin:			
TFSPK-JAN 11	11/1/94	solution #133	2mL
TFSPK-MAR29	29/3/94	Solution #133	2mL
PCBs:			
PCBSPK-JAN11	11/1/94	Solution #48	1mL
		Solution #49	1mL
PCBSPKx0.4-FEB7	7/2/94	PCBSPK-JAN11	40mL
Toxaphene:			
TOXSPK-JAN11	11/1/94	Solution #134	20mL

^ADiluted to total volume of 50 mL.

2.2.3. Preparation of instrument calibration solutions

All calibration solutions were prepared from the intermediate solutions mentioned in sections 2.1 and 2.2.1 as indicated in Table 2.5, diluted with hexane to a final volume of 100 mL. The coding system is similar to that used for the spiking solutions.

Table 2.5: *Preparation of instrument calibration solutions*
 (Diluted to 100 mL with hexane)

Code	Date	Solutions and volumes used	
OC/CB "A":			
OCAINSTx20-NOV15	15/11/93	OCA-NOV15-INT 135TBB-NOV15-INT	20mL 1mL
OCAINSTx10-NOV15	15/11/93	OCA-NOV15-INT 135TBB-NOV15-INT	10mL 1mL
OCAINSTx4-NOV15	15/11/93	OCA-NOV15-INT 135TBB-NOV15-INT	4mL 1mL
OCAINSTx2-NOV15	15/11/93	OCA-NOV15-INT 135TBB-NOV15-INT	2mL 1mL
OCAINSTx2-noIS-NOV15	15/11/93	OCA-NOV15-INT	2mL
OCAINST-NOV15	15/11/93	OCA-NOV15-INT 135TBB-NOV15-INT	1mL 1mL
OCAINSTx0.6-NOV15	15/11/93	OCAINST-noIS-NOV15 135TBB-NOV15-INT	30mL 1mL
OCAINSTx0.2-NOV15	15/11/93	OCAINST-noIS-NOV15 135TBB-NOV15-INT	10mL 1mL
OCAINSTx0.2-noIS-NOV15	15/11/93	OCAINST-noIS-NOV15	10mL
OCAINSTx0.08-NOV15	15/11/93	OCAINSTx0.2-noIS-NOV15 135TBB-NOV15-INT	40mL 1mL
OCAINSTx0.04-NOV15	15/11/93	OCINSTx0.2-noIS-NOV15 135TBB-NOV15-INT	20mL 1mL
OCAINSTx0.02-NOV15	15/11/93	OCAINSTx0.2-noIS-NOV15 135TBB-NOV15-INT	10mL 1mL
OCAINST-MAR30	30/3/94	Solution #146	1mL
OCAINST-MAY26	26/5/94	Solution #146	1mL
OC/CB "B":			
OCBINST-DEC15	15/12/93	OCB-NOV15-INT 135TBB-NOV15-INT	1mL 0.25mL
OCBINST-FEB1	1/2/94	OCB-NOV15-INT 135TBB-NOV15-INT	1mL 0.5mL
OCBINST-MAR22	22/3/94	OCB-NOV15-INT 135TBB-NOV15-INT	1mL 0.5mL
OCBINST-MAY26	26/5/94	OCB-NOV15-INT 135TBB-NOV15-INT	1mL 0.5mL

Table 2.5 (Continued)

Trifluralin:			
TFINST-JAN11	11/1/94	Solution #133	1mL
		135TBB-NOV15-INT	0.5mL
TFINST-MAR29	29/3/94	Solution #133	1mL
		135TBB-NOV15-INT	0.5mL
PCBs:			
PCBINST-JAN11	11/1/94	Solution #48	0.5mL
		Solution #49	0.5mL
		135TBB-NOV15-INT	0.5mL
Toxaphene:			
TOXINST-JAN11	11/1/94	Solution #134	10mL
		135TBB-NOV15-INT	0.5mL

2.3. Extraction procedures and sample preparation

2.3.1. Hexane micro-extraction

All glassware cleaning and QA/QC procedures were as described in method OWOC-E3120B.

2.3.1.1. Recoveries of spiked compounds

In a typical experiment 1 mL of spiking solution was added to each 800 mL sample of water with a 1 mL volumetric pipette. After thorough mixing, the spiked samples were extracted using a small quantity of hexane (usually 2 mL, added to the sample with a volumetric pipette) and rolling the samples (80 rpm) for at least 1 hour. After extraction, the samples were left to settle for 10 minutes. Distilled water was added to each sample to raise the level of the organic phases up to the mouth of the amber bottles. A few drops of acetone were added as necessary to break any emulsions formed. The organic phases were then transferred to GC

vials using disposable pasteur pipettes and analyzed as described in section 2.4.

2.3.1.2. Extraction of Smithville samples

The sample volumes of Smithville samples varied from about 750-950 mLs. One millilitre of internal/surrogate standard solution (100 ng/mL 135-TBB) was added to each sample and all samples were thoroughly mixed. Two millilitres of hexane was added to each sample with a volumetric pipette, and the samples were extracted on rollers for 90 minutes. A measured amount of distilled water was added to each sample to raise the level of the organic phase up to the mouth of the amber bottle. A few drops of acetone were added as necessary to break any emulsions that may have formed. The organic phases were transferred to 2mL GC vials using disposable pasteur pipettes and analyzed as described in section 2.4. Cleanup of the sample extract using mercury as described in method OWOC-E3120B was sometimes required in order to remove sulfur from the extract. The original sample volumes were calculated by subtracting the volume of distilled water added to the sample from the total final sample volume.

2.3.1.3. Experimental variations

Table 2.6 lists the parameters of all hexane micro-extractions performed over the duration of this project. As described below, there were 4 basic variations from the procedures described in sections 2.3.1.1 and 2.3.1.2.

(1) Use of more than one spiking solution per sample:

For recovery studies, OC/CB components and internal/surrogate standard were not necessarily contained in the same spiking solution. When they were not, the OC/CB compounds were first spiked to the sample, which was then thoroughly

mixed. The internal/surrogate standard solution was then added.

(2) Extraction time:

In order to determine required extraction times a preliminary study was conducted in which extraction times were varied from 15 to 90 minutes.

(3) Volume of n-hexane:

To determine the amount of hexane required, a preliminary study was conducted in which hexane volumes varied from 1 mL to 3 mL.

(4) Salting samples:

In experiments to investigate whether salting appreciably improved recoveries of certain spiked compounds, water samples were spiked and thoroughly mixed, sodium chloride (50g or 100g) was added, and the samples were placed on the rollers for 15 minutes. Hexane was then added and extraction took place for at least 1 hour.

2.3.2. Solid phase micro-extraction

All required materials and equipment, which included solid phase micro-extraction fibers of various dimensions, a fiber assembly and manual holder, teflon coated magnetic stir bars, and 40 mL amber glass vials with screw caps containing teflon lined silicone septa, were provided by Professor Janusz Pawliszyn.

Fiber pretreatment conditions, extraction times, desorption times and instrument operating parameters (affected by desorption times) were varied to establish optimum extraction conditions. Details are presented in chapter 7.

Table 2.6: *Experimental parameters for hexane micro-extractions*

Date	Spiking solution(s) used (1 mL)	Number of reps	Volume of hexane (mL)	Extr. time (min)
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Recovery studies^A:

17/11/93	OCASPK-NOV15	5	1	90
17/11/93	OCASPK-NOV15	5	2	90
17/11/93	OCASPK-NOV15	5	3	90
23/11/93	OCASPK-NOV15	5	2	15
23/11/93	OCASPK-NOV15	5	2	30
23/11/93	OCASPK-NOV15	5	2	60
23/11/93	OCASPK-NOV15	5	2	90
16/12/93	OCASPKx0.04-NOV15	5	2	90
16/12/93	OCASPKx0.02-NOV15	5	2	90
16/12/93	OCBSPK-DEC15 135TBB-DEC15-50ng/mL	5	2	90
12/1/94	TFSPK-JAN 11 135TBB-DEC15-50ng/mL ^B	5	2	60
12/1/94	PCBSPK-JAN11 135TBB-DEC15-50ng/mL ^B	5	2	60
12/1/94	TOXSPK-JAN11 135TBB-DEC15-50ng/mL ^B	5	2	60
2/2/94	OCBSPKx0.2-FEB1 135TBB-DEC15-50ng/mL	8	2	90
7/2/94	PCBSPKx0.4-FEB7 135TBB-DEC15-50ng/mL ^B	8	2	60
10/2/94	OCBSPK-DEC15 135TBB-FEB10-100ng/mL	10	2	90
10/2/94	Lakeview treated water OCBSPK-DEC15 135TBB-FEB10-100ng/mL	10	2	90

Table 2.6 (Continued)

12/3/94	OCASPK-NOV15	8	2	60
12/3/94	OCASPKx0.4-MAR12 135TBB-FEB10-100ng/mL	8	2	60
14/3/94	OCASPKx0.02-MAR14 135TBB-FEB10-100ng/mL	8	2	60
15/3/94	OCASPKx0.04-MAR14 135TBB-FEB10-100ng/mL	8	2	90
15/3/94	OCASPKx0.06-MAR14 135TBB-FEB10-100ng/mL	8	2	90
22/3/94	OCBSPK-MAR22 135TBB-FEB10-100ng/mL	8	2	60
22/3/94	Lakeview raw water OCBSPK-MAR22 135TBB-FEB10-100ng/mL	9	2	60
23/3/94	OCBSPKx0.4-MAR22 135TBB-FEB10-100ng/mL	8	2	60
25/3/94	OCBSPK-MAR22 135TBB-FEB10-100ng/mL	8	2	60
25/3/94	OCBSPK-MAR22 135TBB-FEB10-100ng/mL (salted - 50g NaCl)	4	2	60
25/3/94	OCBSPK-MAR22 135TBB-FEB10-100ng/mL (salted - 100g NaCl)	4	2	60
29/3/94	TFSPK-MAR29 135TBB-FEB10-100ng/mL	8	2	60
29/3/94	TFSPK-MAR29 135TBB-MAR29-100ng/mL (salted - 50g NaCl)	4	2	60
29/3/94	TFSPK-MAR29 135TBB-MAR29-100ng/mL (salted - 50g NaCl)	4	2	60
31/3/94	Verner raw water: OCASPK-MAR30 (salted: 100g NaCl)	10	2	60
31/3/94	Verner treated water: OCASPK-MAR30 (salted: 100g NaCl)	10	2	60

Table 2.6 (Continued)

31/3/94	Verner raw water: OCBSPK-MAR22 135TBB-MAR29-100ng/mL (salted: 100g NaCl)	9	2	60
31/3/94	Verner treated water: OCBSPK-MAR22 135TBB-MAR29-100ng/mL (salted: 100g NaCl)	9	2	60
20/4/94	Lakeview raw water OCASPK-MAR30	10	2	90
20/4/94	Lakeview treated water OCASPK-MAR30	10	2	90
7/5/94	OCBSPKx0.12-MAY3 135TBB-MAR29-100ng/mL	8	2	90
7/5/94	OCBSPKx0.8-MAY3 135TBB-MAR29-100ng/mL	8	2	90
8/5/94	OCBSPKx0.08-MAY3 135TBB-MAR29-100ng/mL	8	2	90
9/5/94	OCBSPKx0.04-MAY3 135TBB-MAR29-100ng/mL	8	2	90
2/6/94	OCASPKx0.8-MAY26 135TBB-MAY26-100ng/mL	8	2	90
2/6/94	OCASPKx0.1-MAY26 135TBB-MAY26-100ng/mL	8	2	90
3/6/94	OCASPKx0.4-MAY26 135TBB-MAY26-100ng/mL	8	2	90
3/6/94	OCASPKx0.2-MAY26 135TBB-MAY26-100ng/mL	8	2	90
6/6/94	OCASPKx0.08-MAY26 135TBB-MAY26-100ng/mL	8	2	90
6/6/94	OCASPKx0.04-MAY26 135TBB-MAY26-100ng/mL	8	2	90
8/6/94	OCBSPKx0.2-MAY26 135TBB-MAY26-100ng/mL	8	2	90
9/6/94	OCBSPKx0.8-MAY26 135TBB-MAY26-100ng/mL	8	2	90
10/6/94	OCBSPKx0.4-MAY26 135TBB-MAY26-100ng/mL	8	2	90

Table 2.6 (Continued)

10/6/94	OCBSPKx0.1-MAY26 135TBB-MAY26-100ng/mL	8	2	90
14/6/94	OCBSPK-MAY26 ^c	8	2	90
14/6/94	Verner raw water ^c OCBSPK-MAY26	8	2	90
6/7/94	OCASPK-MAY26 ^c	8	2	90
6/7/94	Verner raw water ^c OCASPK-MAY26	8	2	90

Analysis of Smithville samples^c:

21/7/94	Smithville 34D18 135TBB-JUL21-100ng/mL	8	2	90
26/7/94	Smithville 29S12 135TBB-JUL21-100ng/mL	8	2	90
27/7/94	Smithville RWS8 135TBB-JUL21-100ng/mL	8	2	90
9/8/94	Smithville RWS8 135TBB-JUL21-100ng/mL	13	2	90
9/8/94	Smithville 29S12 135TBB-JUL21-100ng/mL	10	2	90
18/8/94	Smithville RWS8 135TBB-JUL21-100ng/mL (salted: 100g NaCl)	14	2	90

- A: From distilled or HPLC grade water, unless otherwise indicated.
- B: Two millilitres.
- C: An equal number of extractions was also performed by method OWOC-E3120B.

2.4. Instrumental analysis

2.4.1. Equipment

All analyses of sample extracts were performed with a Varian 3400 gas chromatograph, equipped with dual ^{63}Ni electron capture detectors, a split/splitless injector and Varian 8100 autosampler.

The HRGC columns were fused silica DB-1 and DB-1701 purchased from J&W Scientific inc. Both had dimensions of 30 m x 0.25 mm i.d. with $d_f = 0.25\ \mu\text{m}$. Both columns were inserted in the injection port through a 2-hole graphitized VespelTM ferrule and thus the sample extracts could be introduced to both columns simultaneously. Each column led to a separate detector, such that DB-1 corresponded to the "channel 1" and DB-1701 corresponded to the "channel 2" signals, interfaced to the data station.

2.4.2. Instrument parameters.

2.4.2.1. Gas supply

Autosampler: Air, extra dry,
charcoal gas trap,
80 psi.

Carrier gas: Helium, ultra high purity,
charcoal/molecular seive/oxygen gas trap,
column head pressure of 20 psi

Make-up gas: Nitrogen, ultra high purity,
charcoal/molecular seive/oxygen gas trap,
30 mL/min.

2.4.2.2. Basic GC parameters

Injector temp: 250°C
Sample injection volume: 2.2 μL
Septum purge: 2 mL/min
Split flow: 50 mL/min
Splitter relay settings:
off: 0.00 min

on: 0.25 min

off: 2.00 min

Column temperature program:

80°C (2 min), 4°C/min to 270°C (4 min)

Detector temp: 330°C

2.4.2.3. Details of GC configuration inputs

Part 1: Times and Date.

Thermal stabilize time: 2 min

Time of day (HH, MM)

Date (Day, Month)

Year

Coolant timeout in min: INF

Part 2: Temperature Limits.

Column temp limit: 280°C

Injector temp limit: 260°C

Auxiliary temp limit: 52 (default)

Detector temp limit: 350°C

Column standby temp: 80°C

Enable column standby temp? No

Part 3: Set check for GC ready.

Wait for temp ready? Yes

Wait for aux temp ready? No

Wait for det temp ready? Yes

Wait for ext. device ready? No

Wait if faults present? Yes

Initial relays at run end? Yes

Part 4: Set lock code? (No)

Part 5: Turn hardware on/off.

Det A on? Yes

Det B on? Yes

Det oven on? Yes

Inj. oven on? Yes

Aux oven on? No

Coolant to column? No

Part 6: Other configurations.

A/S fast injection rate in $\mu\text{L}/\text{sec}$: 5.0

A/S slo injection rate in $\mu\text{L}/\text{sec}$: 1.0

A/S vial needle depth (%): 90

A/S solvent select: 1
 A/S air dry after wash? No
 A/S upper air gap? Yes
 A/S lower air gap? Yes
 A/S viscosity factor: 1
 A/S/ start at rack1 vial1? Yes
 A/S hot needle time (min): 0
 next run number: (reset to 1 before each analysis series)
 sound keystrokes? Yes

Part 7: GC method parameters.

Initial column temp: 80 °C
 Initial column hold time: 2 min
 PRGM1 final column temp: 270 °C
 PRGM1 col rate in °C/min: 4
 PRGM1 hold time: 4 min
 Add next colum program? No
 Injector temp: 250 °C
 Detector temp: 330 °C
 Detector A or B? A
 ECD A initial attenuation: 8
 ECD A initial range: 1
 ECD A autozero on? Yes
 Time program ECD A? No
 ECD B initial attenuation: 8
 ECD B initial range: 1
 ECD B autozero on? Yes
 Time program ECD AB No
 A/S vial mode: Multi
 A/S sample volume in µL: 2.2
 A/S solvent plug size in µL: 0.1
 Fast injection rate? Yes
 A/S injection time in min: 0.03
 A/S wait for ready? Yes
 Number inj/Calib vial: 1
 Number inj per analysis vial: 1
 Sample table? No
 Initial relays: 1
 PRGM1 relay time in min: 0.25
 PRGM1 relays: -1
 PRGM2 relay time in min: 2
 PRGM2 relays: 1
 Add next realy PRGM? No
 Add integration section? No
 Add time events section? No
 Add peak table section? No
 Method complete - End time 53.50

2.4.3. Data aquisition and manipulation using Chrom Perfect™

Chrom perfect™ (Justice Innovations Inc.) method files consist of ten modules each of which controls a specific data aquisition or manipulation function. Unless otherwise specified, all calculations were based on internal standard calibration with respect to 1,3,5-Tribromobenzene, the same compound which served as a surrogate standard in all hexane micro-extractions.

Six Chrom perfect™ method files were used for the analysis of OC/CB compounds and PCBs to automatically acquire and process raw data from channels 1 and 2. Sequence tables were created for each series of analyses, which specified which of the methods should be used for a given sample vial number.

The following shows a listing of the key method modules and parameters:

Aquire Module (data aquisition)

Run time:	53.5 minutes
Sampling rate:	10/second
Binary area files:	Yes
Bind results to raw file:	Yes
Voltage range:	1volt
1 or 2 channel aquisition:	2

Integ Module (integration)

Peak threshold:	0
Peak width:	0.05 minutes

Events Module (times events)

0.10 minutes relay 1	open
0.25 minutes relay 2	closed
2.00 minutes relay 2	open
53.5 minutes relay 1	closed

Cal Module (calibration file specification)

Calibration files:

channel 1 (DB-1): Iris1.cal (OC "A"), Iris2.cal (OC "B")
channel 2 (DB-1701): Iris1B.cal (OC "A"), Iris2B.cal (OC "B")
Calibration type: Internal/single point
Fit: linear/equal weighting
Quantitation: area
Search window: 0.1 minutes
Peak area reject: 5000

Report (report format)

Fixed format: No
Format file name: Iris1.fmt, Iris2.fmt (DB-1)
Iris1B.fmt, Iris2B.fmt (DB-1701)

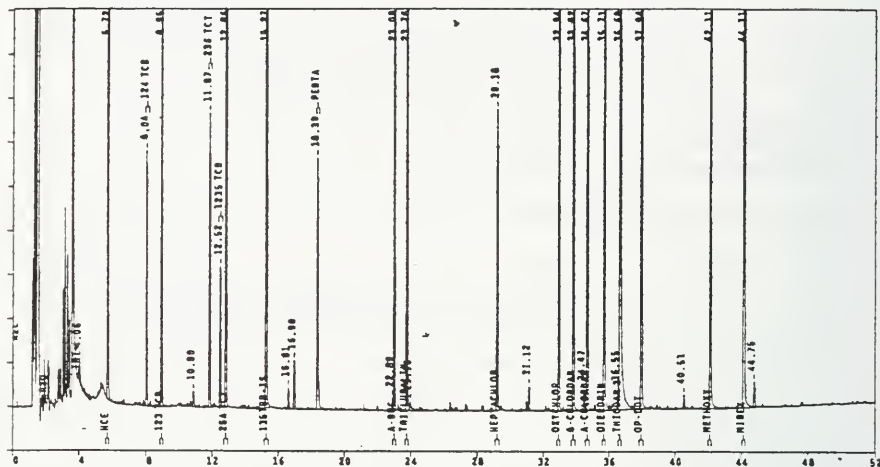
Plot (chromatogram plots)

Automatic zeroing/scaling: no
Low/High scale: -5/50 mV
Plot start/stop: 0/53.5 min
Panel/number/orientation: 1/horizontal
Plot width/height: 7.5/4.0 inches
Omit baseline/peaknames: no

2.4.4. Sample chromatograms of OC/CB compounds

Examples of chromatograms and report outputs that were obtained for calibration standards containing OC/CB "A" and OC/CB "B" compounds are shown in Figures 2.1 to 2.4.

File=C:\CP\DATA1\IRIS08.04R Date printed=04-08-1994 Time= 19:07:13
 Sample Name=STD A
 0.0 to 52.0 min. Low Y=-5.0 High Y=50.0 mv Span=55.0



R&D MICROEXTRACTION/ANALYSIS OF OC/CB PESTICIDES
 VARIAN 3400 ECD COLUMN DB1
 STD ADIL FACT 1 ANALYZED: Apr 8, 1994 19:06:54
 METHOD: C:\CP\DATA1\IRIS1.METCAL FILE: C:\CP\DATA1\IRIS1.CALFILE: C:\CP\DATA1\IRIS08.04R

Amount (ng/L)	Peak Name	Amount Ng/L	Ret Time (min)	Time Offset	Peak Area	Peak Out of Type Bound
10.0404	HCE	10.0	5.717	-0.001	276605	BB
50.2933	124 TCB	50.3	8.044	0.001	81646	VV
50.5098	123 TCB	50.5	8.950	0.001	162659	VB
50.3786	236 TCT	50.4	11.873	0.001	112234	VV
10.0516	1235 TCB	10.1	12.521	0.001	50742	BV
51.2817	26A TCT	51.3	12.856	0.002	569473	BB
50.0000	135TBB-IS	50.0	15.273	0.002	891123	BB
10.6437	PENTA	10.6	18.386	0.002	116236	VV
10.0560	A-BHC	10.1	23.002	0.000	214521	VV
53.0950	TRIFLURALIN	53.1	23.761	0.002	277156	VV
10.1660	HEPTACHLOR	10.2	29.180	0.002	126903	BV
20.6779	OXYCHLOR	20.7	32.943	0.000	290551	BV
19.9284	G-CHLORDAN	19.9	33.823	0.003	390653	BV
19.9734	A-CHLORDAN	20.0	34.671	0.004	388548	VV
21.0165	DIELDRIN	21.0	35.708	0.004	336101	BV
40.9033	THIODAN 2	40.9	36.675	0.004	697219	VV
52.4105	OP-DDT	52.4	37.944	0.001	480433	VV
53.9214	METHOXY	53.9	42.106	0.000	292479	VV
50.4151	MIREX	50.4	44.113	0.003	636391	BV

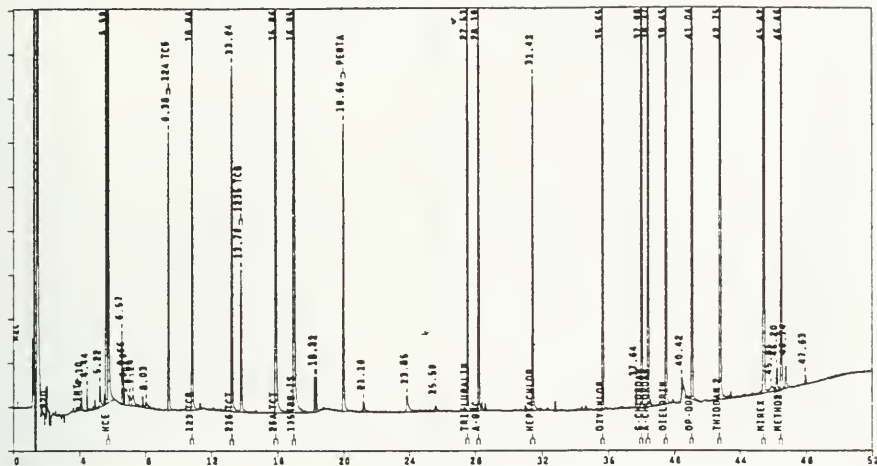
Checked by _____ Date _____

Figure 2.1: Channel 1 (DB-1) output of instrument calibration standard OC/CB "A"

File=C:\CP\DATA1\IRIS08B.04R Date printed=04-08-1994 Time= 19:08:43

Sample Name=STD A

0.0 to 52.0 min. Low Y=-5.0 High Y=50.0 mv Span=55.0



R&D MICROEXTRACTION AND ANALYSIS OF OC-CB PESTICIDES

VARIAN 3400 ECD DB1701 COLUMN

STD ADIL FACT 1 ANALYZED: Apr 8, 1994 19:06:54

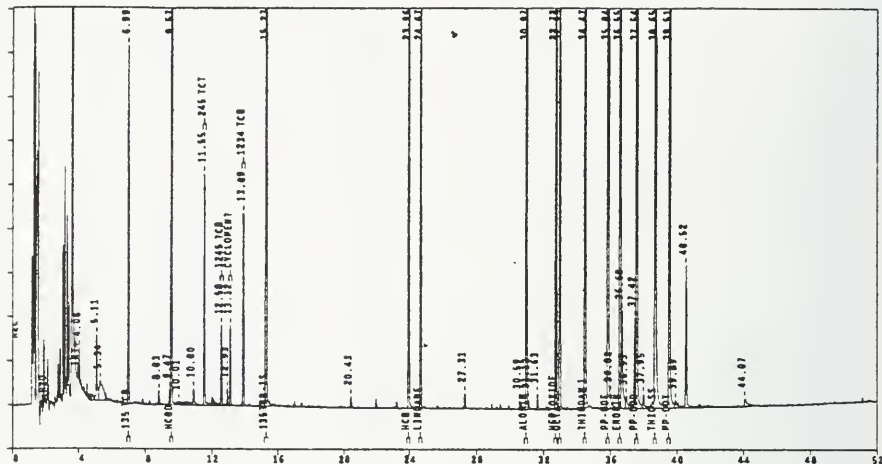
METHOD: C:\CP\DATA1\IRIS1B.NETCAL FILE: C:\CP\DATA1\IRIS1B.CALFILE: C:\CP\DATA1\IRIS08B.04R

Amount (ng/L)	Peak Name	Amount Ng/l	Ret Time (min)	Time Offset	Peak Area	Peak Out of Type Bound
9.6884	HCE	9.7	5.743	-0.001	265069	VB
49.8646	124 TCB	49.9	9.381	0.000	108289	BB
49.9819	123 TCB	50.0	10.837	0.000	196624	BB
50.4794	236 TCT	50.5	13.239	0.001	144500	BV
10.1634	1235 TCB	10.2	13.791	-0.000	65579	VV
51.8155	26A TCT	51.8	15.861	0.002	546968	BV
50.0000	135TBB-IS	50.0	16.945	0.002	781918	VB
9.9346	PENTA	9.9	19.962	-0.000	132522	BB
52.9049	TRIFLURALIN	52.9	27.532	0.003	230843	VV
9.8810	A-BHC	9.9	28.190	-0.000	199038	VV
10.1849	HEPTACHLOR	10.2	31.433	-0.001	158226	VV
20.2983	OXYCHLOR	20.3	35.654	-0.003	270270	VB
19.8589	G-CHLORDAN	19.9	37.983	-0.003	343684	BV
19.8204	A-CHLORDAN	19.8	38.375	-0.004	335741	SBB
20.5372	DIELDRIN	20.5	39.447	0.001	297406	VV
49.7970	OP-DDT	49.8	41.035	-0.000	388369	BB
39.9065	THIODAN 2	39.9	42.753	-0.002	588033	VV
50.0561	MIREX	50.1	45.418	-0.003	513702	VV
52.7956	METHOXY	52.8	46.461	-0.001	168603	VB

Checked by _____ Date _____

Figure 2.2: Channel 2 (DB-1701) output of instrument calibration standard OC/CB "A"

File=C:\CP\DATA1\IRIS323.06R Date printed=03-23-1994 Time= 23:14:57
Sample Name=STD-B
0.0 to 52.0 min. Low Y=-5.0 High Y=50.0 mv Span=55.0



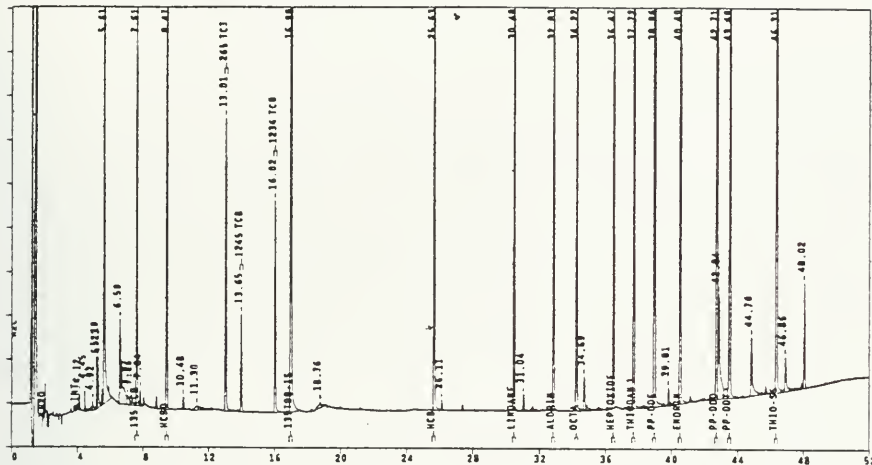
R&D DWA-PHU OC/CB PESTICIDES ANALYSIS BY MICROEXTRACTION
VARIAN 3400 ECD GC DB1 COLUMN
STD-B DIL FACT 1 ANALYZED: Mar 23, 1994 23:14:44
METHOD: C:\CP\DATA\1\IRIS2.NETCAL FILE: C:\CP\DATA\1\IRIS2.CAL FILE: C:\CP\DATA\1\IRIS23.06R

Amount ng/L	Peak Name	Amount Ng/l	Ret Time (min)	Time Offset	Peak Area	Peak Type	Out of Bound
49.5130	135 TCB	49.5	6.994	-0.001	108003	BB	
10.2618	HCBDD	10.3	9.573	-0.003	300155	SBB	
49.5665	245 TCT	49.6	11.546	-0.004	88320	BV	
10.3882	1245 TCB	10.4	12.576	-0.006	31962	VV	
21.0703	CYCLOPENT	21.1	13.121	-0.007	30093	VB	
9.8764	1234 TCB	9.9	13.895	-0.006	73350	VB	
50.0000	135TBB-IS	50.0	15.273	-0.006	1093428	SBB	
9.9906	HCB	10.0	23.958	-0.011	186330	VV	
9.9619	LINDANE	10.0	24.665	-0.014	211311	VV	
10.0562	ALDRIN	10.1	30.975	-0.017	220366	VV	
9.9107	HEPTOXIDE	9.9	32.727	-0.016	194062	VV	
9.9663	OCTA	10.0	32.954	-0.016	242367	VV	
19.8531	THIODAN 1	19.9	34.473	-0.018	409540	BB	
49.6935	PP-DDE	49.7	35.845	-0.014	1018206	VV	
40.5226	ENDRIN	40.5	36.551	-0.004	484027	VV	
49.6352	PP-DDD	49.6	37.540	-0.010	713924	VV	
39.7668	THIO-SS	39.8	38.645	-0.018	585381	VV	
48.9230	PP-DDT	48.9	39.505	-0.022	634918	VV	

Checked by _____ Date _____

Figure 2.3: Channel 1 (DB-1) output of instrument calibration standard OC/CB "B"

/file=C:\CP\DATA1\IRIS323B.06R Date printed=03-23-1994 Time= 23:16:17
 Sample Name=STD-B
 0.0 to 52.0 min. Low Y=-5.0 High Y=50.0 mv Span=55.0



R&D DWA-PHU OC/CB PESTICIDES ANALYSIS BY MICROEXTRACTION
 VARIAN 3400 ECD GC DB1701 COLUMN
 STD-BDIL FACT 1 ANALYZED: Mar 23, 1994 23:14:44
 METHOD: C:\CP\DATA1\IRIS2B.METHOD FILE: C:\CP\DATA1\IRIS2B.CAL FILE: C:\CP\DATA1\IRIS323B.06R

Peak #	Peak Name	Amount ng/L	Ret Time (min)	Time Offset	Peak Area	Peak Out of Type Bound
14	135 TCB	49.70987	7.612	-0.002	143317	VV
18	HCB	10.06764	9.465	-0.004	256950	BB
24	245 TCT	49.78848	13.009	-0.010	118215	BV
27	1245 TCB	10.05495	13.945	-0.011	40452	VB
29	1234 TCB	10.01027	16.022	-0.014	90321	BB
30	135TBB-IS	50.00000	16.983	-0.017	945128	BB
36	HCB	10.09712	25.634	-0.022	191726	BV
40	LINDANE	10.14543	30.478	-0.026	203804	BB
45	ALDRIN	10.13844	32.834	-0.027	208018	BB
47	OCTA	10.29857	34.218	-0.025	223745	SBB
51	HEPTOXIDE	10.12553	36.474	-0.027	183332	BB
54	THIODAN 1	20.50152	37.716	-0.028	368592	SBB
56	PP-DDE	50.49198	38.957	-0.030	899877	SBB
60	ENDRIN	40.53137	40.495	-0.029	398309	BB
65	PP-DDD	50.69347	42.705	-0.034	612574	VV
67	PP-DDT	50.60149	43.488	-0.032	431150	VV
73	THIO-SS	40.78742	46.307	-0.035	455105	VV

Checked by _____ Date _____

Figure 2.4: Channel 2(DB-1701) output of instrument calibration standard OC/CB "B"

3. Preliminaries

3.1. General comments

Before beginning with recovery studies of hexane micro-extraction, it was first necessary to determine the optimal extraction parameters of time and volume of hexane. Also, since the instrument used for this project is not one that is used for routine analyses, instrument performance had to be assessed. Instrument performance was evaluated according to the criteria outlined in method OWOC-E3120B.

3.2. Instrument performance

3.2.1. Linearity

Instrument linearity was established by monitoring the average of the two detector responses (as peak area counts) towards the OC/CB "A" compounds for 10 different dilutions of a concentrated stock solution. Table 3.1 lists the concentrations of each of the components in these solutions. Details of the preparation of the solutions are given in Table 2.5 (p.19). Combined scatter plots of detector response versus compound concentration are shown in Figure 3.1. Plots for each individual compound are in Appendix 1. The observed linear dynamic ranges for each compound are listed in Table 3.2, and for purposes of comparison, the values presented in method OWOC-E3210B are also listed. These results show that the linear dynamic ranges for the OC/CB "A" compounds are similar to those demonstrated by the instruments used for routine analysis. It is assumed that linearity for all the other target compounds are also comparable.

Table 3.1: Concentration ranges of OC/CB "A" components for the determination of instrument linearity.

Solution*-->	A	B	C	D	E	F	G	H	I	J
Compound	Concentration (ng/mL)									
HCE 1235-TCB PENTA α -BHC Heptachlor	0.2	0.4	0.8	2	6	10	20	40	100	200
Oxychlor γ -Chlordane α -Chlordane Dieldrin	0.4	0.8	1.6	4	12	20	40	80	200	400
Thiodan-2	0.8	1.6	3.2	8	24	40	80	160	400	800
123-TCB 124-TCB 236-TCT 26 α -TCT op'-DDT Methoxychlor MIREX	1	2	4	10	30	50	100	200	500	1000

* Solutions as described in Table 2.5 (p.19):

A: OCAINSTx0.02-NOV15
 B: OCAINSTx0.04-NOV15
 C: OCAINSTx0.08-NOV15
 D: OCAINSTx0.2-NOV15
 E: OCAINSTx0.6-NOV15
 F: OCAINST-NOV15
 G: OCAINSTx2-NOV15
 H: OCAINSTx4-NOV15
 I: OCAINSTx10-NOV15
 J: OCAINSTx20-NOV15

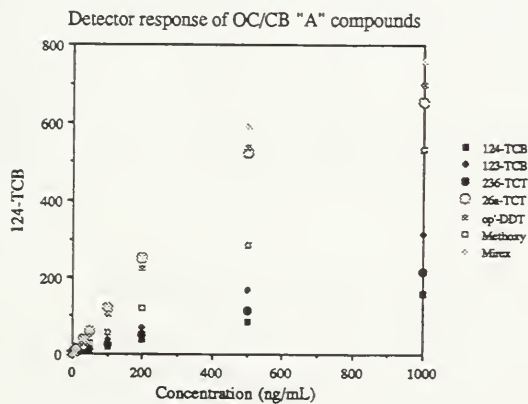
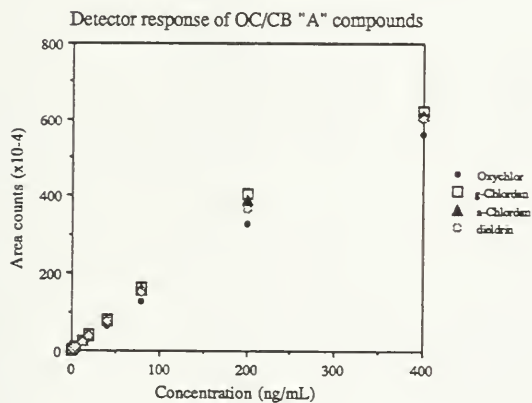
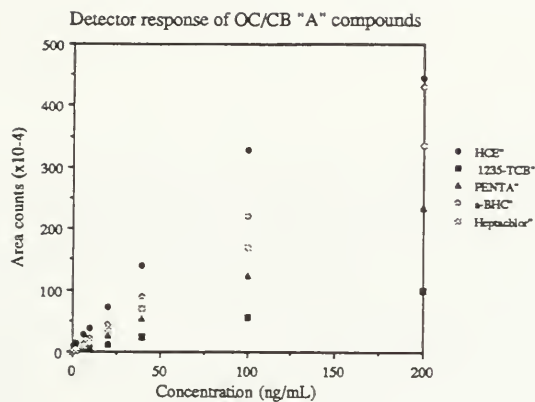


Figure 3.1: *Detector response versus concentration for OC/CB "A" compounds*

Table 3.2: *Linear dynamic range for OC/CB "A" compounds*

Compound	Linear dynamic range (ng/mL)	
	Observed	Reported in OWOC-E3210B
Hexachloroethane	0.2-100	1-100
1,2,3,5-Tetrachlorobenzene	0.2-100	1-100
Pentachlorobenzene	0.2-200	1-100
α -BHC	0.2-200	1-100
Heptachlor	0.2-200	1-100
Oxychlor	0.4-200	2-200
γ -Chlordane	0.4-200	2-200
α -Chlordane	0.4-200	2-200
Dieldrin	0.4-200	2-200
Thiodan-2	0.8-300	4-400
1,2,3-Trichlorobenzene	1-1000	5-500
1,2,4-Trichlorobenzene	1-1000	5-500
2,3,6-Trichlorotoluene	1-1000	5-500
2,6,a-Trichlorotoluene	1-300	5-500
o,p'-DDT	1-500	5-500
Methoxychlor	1-1000	5-500
Mirex	1-500	5-500

3.2.2. Within-run instrument precision

Instrument precision was established by injecting 8 replicates of each of OC/CB calibration solutions OCAINST-MAY26 and OCBNST-MAY26, and 10 replicates of PCB calibration solution PCBINST-JAN11. Each of the compounds were quantified by internal standard calibration, whereby 50 ng/mL of 1,3,5-Tribromobenzene was used in all calibration solutions as the

internal standard. Results are presented in Table 3.3 along with those given in method OWOC-E3120B. Comparison of the results confirms that the use of internal standard tends to improve both accuracy (average result closer to 100%) and precision (lower relative standard deviation, RSD).

Table 3.3: *Instrument precision*

Compound	Conc. (ng/mL)	Observed		Reported in OWOC-E3210B	
		Ave result (%)	RSD (%)	Ave result (%)	RSD (%)
HCE	10	101	2.5	101	2.3
124-TCB	50	100	0.76	100	2.9
123-TCB	50	100	0.44	100	2.7
236-TCT	50	100	0.74	100	2.4
1235-TCB	10	100	1.7	100	2.0
26 α -TCT	50	99	0.62	99	3.4
Penta	10	102	4.7	103	3.3
α -BHC	10	101	1.7	100	2.1
Trifluralin	50	99	0.72	103	3.8
Heptachlor	10	98	2.4	101	2.4
Oxychlor	20	100	1.3	100	2.0
γ -Chlordan	20	101	1.4	101	2.2
α -Chlordan	20	101	1.4	97	2.2
Dieldrin	20	101	1.4	98	2.6
Thiodan-2	40	102	2.0	97	2.8
op'-DDT	50	101	1.4	100	2.6
Methoxy	50	101	1.6	106	4.9
Mirex	50	102	2.2	102	2.4

Table 3.3 (Cont'd)

135-TCB	50	100	1.6	99	2.6
HCBD	10	100	0.7	99	2.1
245-TCT	50	99	1.0	102	2.2
1245-TCB	10	100	1.1	100	2.0
1234-TCB	10	100	1.3	101	2.1
HCB	10	100	2.7	98	1.9
Lindane	10	100	1.3	99	2.1
Aldrin	10	100	2.1	96	2.3
Heptoxide	10	100	2.8	99	2.9
Octa	10	100	2.9	99	1.8
Thiodan-1	20	100	3.2	98	2.7
pp'-DDE	50	100	4.0	101	1.9
Endrin	40	100	4.0	98	2.4
pp'DDD	50	101	4.4	101	2.1
Thio-SS	40	101	4.8	99	2.3
pp'-DDT	50	101	4.6	99	2.5
PCBs	100	101	1.3	104	4.0

3.3. Extraction parameters

3.3.1. Volume of hexane required

In a previous study, 500 to 800 mL samples of spiked water were extracted with 1-3 mL volumes of hexane²⁸. There it was reported that unacceptable over-recoveries were observed when low volumes (1-2 mL) of hexane were used in the extraction experiments, while increasing the extracting volume of hexane to 3 mLs reduced the degree of over recovery²⁸. This contradicts the theory of liquid-liquid extraction, and

therefore similar experiments were repeated to verify this observation.

Fifteen 800 mL samples of distilled deionized water were spiked with 1 mL of solution containing the OC/CB "A" compounds (OCASPK-NOV15 from Table 2.4). The compounds were extracted with 1, 2, or 3 mLs of hexane for 90 minutes. Five replicates were prepared for each volume of hexane used. A reagent blank was prepared in which 1 mL of acetone was added to a water sample and extracted with 2 mLs hexane. Samples extracts were transferred to GC vials and analyzed by external standard and internal standard methods of quantitation. For the latter, the internal standard used was 100 ng 1,3,5-Tribromobenzene which was introduced to the sample as a surrogate standard. More details are presented in section 3.3.3.

Percent recoveries and standard deviations are listed in Table 3.4. Difficulties were encountered in recovering the hexane layer when only 1 mL extraction volumes were used. In most cases not enough was obtained for analysis. Therefore, only duplicate results were obtained for the 1 mL replicates.

Statistical comparisons were made between the recoveries observed for each compound with 1, 2 and 3 mLs hexane. This was accomplished by analysis of variance (ANOVA) at 99% confidence²⁹. The results of this analysis is presented in Table 3.5. With the external standard quantitation method, in all but two cases there were no significant differences in recovery. The two exceptions were HCE and 236-TCT, and in these cases no obvious trends were observed in the way that the recoveries differed as a function of hexane volume (refer to Table 3.3). With the internal standard quantitation method, there was a higher incidence of statistically significant differences in recoveries, due to the improvement in precision (section 3.3.3.). However, again there were no consistent trends between these compounds in the the way that the recoveries differed as a function of hexane volume. Thus,

these data do not support the previous observation that recoveries are lowered by increasing the volume of hexane.

All remaining work in this project was based on 2 mL hexane extractions. This volume was chosen in order to match the final volume of sample extract which is specified in method OWOC-E2310B, thereby providing a simple means of comparing detection limits.

Table 3.4: *Average percent recoveries of spiked OC/CB "A" compounds in distilled deionized water, extracted with 1, 2, or 3 mLs hexane. (Standard deviations in parentheses).*

Compound	Percent recovery and standard deviation					
	External standard method			Internal standard method (1,3,5-TBB)		
	1 mL	2 mL	3 mL	1 mL	2 mL	3 mL
HCE	88	90 (5)	80.5 (2)	86	88 (4)	88.5 (2)
124-TCB	102	110 (4)	103 (4)	89	103 (3)	100 (1)
123-TCB	103	109 (4)	101 (4)	94	102 (2)	105 (1)
236-TCT	99	108 (5)	95 (4)	95	102 (2)	103.4 (0.6)
26A-TCT	107	107 (5)	97 (4)	101	101 (1)	102.4 (0.5)
1235-TCB	108	110 (5)	105 (4)	94	102.5 (0.5)	103.0 (0.5)
Penta	91	100 (5)	90 (5)	86	92 (2)	96 (4)
a-BHC	110	105 (5)	96 (4)	107	102 (1)	103.0 (0.5)
Hepta	104	90 (10)	99 (4)	107	90 (5)	96 (2)
Oxychlor	105	95 (10)	102 (5)	93	90 (5)	102 (2)
g-Chlordan	106	92 (10)	100 (5)	95	92 (5)	101 (2)
a-Chlordan	105	95 (10)	98 (5)	96	90 (5)	102 (2)
Dieldrin	116	108 (5)	105 (5)	108	105 (2)	109 (2)
Thiodan-2	121	109 (5)	102 (9)	86	106 (4)	102 (8)
op' -DDT	117	86 (10)	99 (5)	102	84 (6)	99 (4)
Methoxy	124	101 (6)	115 (10)	102	104 (2)	106 (8)
Mirex	109	99 (10)	101 (6)	98	95 (6)	103 (3)

Table 3.5: Results of ANOVA evaluation on differences in recoveries of OC/CB "A" compounds while changing the volumes of hexane used.

Compound	Significant difference ?	
	External standard quantitation	Internal standard quantitation
HCE	Yes	No
124-TCB	No	Yes
124-TCB	No	Yes
236-TCT	Yes	Yes
26 α -TCT	No	Yes
1235-TCB	No	Yes
Penta	No	Yes
α -BHC	No	No
Heptachlor	No	No
Oxychlor	No	No
γ -chlordan	No	No
α -chlordan	No	Yes
Dieldrin	No	No
Thiodan-2	No	No
op'-DDT	No	Yes
Methoxy	No	No
Mirex	No	No

3.3.2. Time required for extraction

In order to determine the time required for extraction, 20 samples of distilled deionized water were spiked with 1 mL of a solution containing OC/CB "A" compounds (OCASPK-NOV15, see Table 2.4). All samples were extracted with 2 mLs hexane.

Five samples each were extracted for 15, 30, 60 and 90 minutes. Combined scatter plots of peak area versus time of extraction are shown in Figure 3.2. In general the magnitudes of the peak areas levelled out to a maximum value after 60 minutes. Thus, all subsequent extractions for this project were performed for a minimum of 60 minutes.

3.3.3. The use of 1,3,5-Tribromobenzene (135-TBB) as internal/surrogate standard

For all hexane micro-extractions a certain known amount (usually 100 ng) of 1,3,5-Tribromobenzene was spiked to each sample and used as a recovery (surrogate) standard. The recovery of each individual compound was adjusted to that of the surrogate by using it as the internal standard in quantitation.

Although the use of a surrogate compound in internal standard calculations is a contentious issue, since it is probably not realistic to expect the recoveries of all compounds to be represented by the surrogate, this method is useful in correcting for instrumental fluctuations and variations that might occur in the sample preparation steps. In contrast, the external standard method relies on accurate measurement of the final volume of sample extract, consistent volumes injected into the GC, and stable detector response. Accuracy and precision are lowered as a result of the propagation of errors generated from these sources. This is exemplified by the within-run instrument precision data presented earlier in Table 3.3, and now in Table 3.6, which lists the 99% confidence intervals of pooled results from the experiments described in section 3.3.1. In most cases the internal standard method provided better accuracy (% recovery closer to target) and always gave higher precision (narrower confidence intervals).

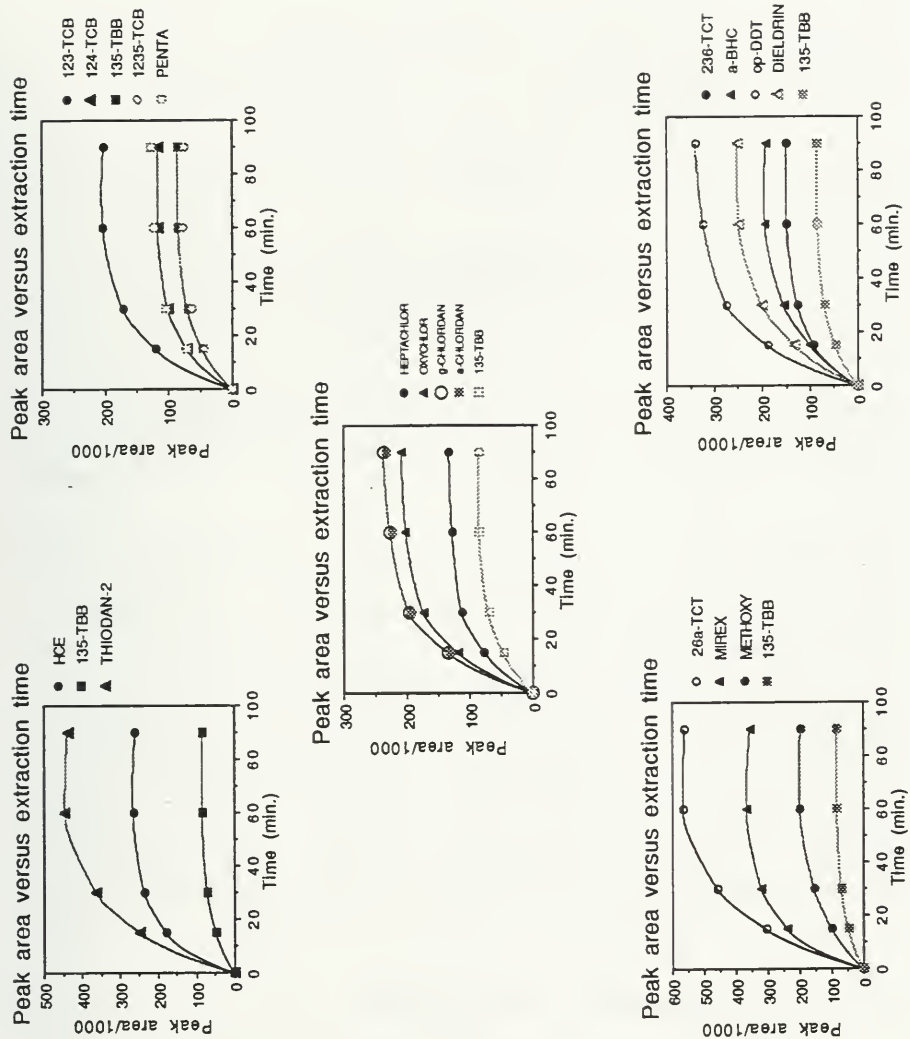


Figure 3.2: Area counts versus time of extraction for OC/CB "A" compounds.

Table 3.6: *Confidence intervals of percent recoveries
(n = 12, 99% confidence level)*

Compound	External standard method		Internal standard method	
	Recovery (%)	Confidence interval	Recovery (%)	Confidence interval
HCE	86	81-91	88	86-90
124-TCB	106	102-110	100	95-104
123-TCB	105	100-109	102	99-105
236-TCT	102	96-107	101	99-104
26 α -TCT	103	97-108	101	100-102
1235-TCB	108	104-111	101	99-104
Penta	93	88-98	93	89-96
α -BHC	103	97-109	103	102-105
Heptachlor	96	89-103	96	86-105
Oxychlor	99	93-106	96	91-101
γ -Chlordan	97	90-105	96	91-101
α -Chlordan	98	91-104	96	90-101
Dieldrin	107	102-113	106	104-109
Thiodan-2	108	101-115	105	101-110
op'-DDT	96	86-107	95	87-103
Methoxy	111	101-120	105	101-109
Mirex	102	95-108	99	94-103

3.4. Extraction efficiency

Six distilled deionized water samples, three spiked with OC/CB "A" compounds and three with OC/CB "B" compounds were first extracted by the hexane micro-extraction procedure. After removing the hexane layer for analysis, the residual analyte in each sample was further extracted using method

OWOC-E3120B. Care was taken that the final extract volumes for the first and second extractions were equal, which permitted calculation of extraction efficiency of the hexane micro-extraction procedure (relative to that of the current method) based on peak area counts of each compound in both extracts as follows:

$$\text{efficiency (\%)} = \frac{\text{Peak area (hexane)}}{\text{Peak area (hexane + residual)}} \times 100$$

The average extraction efficiencies observed for each individual compound ranged from 82-100%. They are listed in Table 3.7.

3.5. Summary

The preliminary experiments described in sections 3.2 through 3.4 provide the foundation of all subsequent experiments to validate the hexane micro-extraction method.

In section 3.2 it was shown that the instrument used for this research performs adequately compared to those used for routine analysis. Section 3.3 describes how the extraction parameters of time (at least 60 minutes) and volume (2 mL hexane) were justified. The method of internal standard quantitation was selected because this yields superior accuracy and precision, as shown by the data presented in Tables 3.3, 3.4 and 3.6. The calculation is based on detector response of all compounds relative to 1,3,5-Tribromobenzene, which is added to each sample as a surrogate standard. Comparison of the behaviour of this compound to the other analytes in the time profiles (Figure 3.2) and extraction efficiency measurements (Table 3.7) justifies this practice.

Table 3.7: Measured extraction efficiency of hexane micro-extraction method.

OC/CB "A" compounds		OC/CB "B" compounds	
name	average extraction efficiency (%)	name	average extraction efficiency (%)
HCE	97	135-TCB	97
124-TCB	97	HCBD	97
123-TCB	96	245-TCT	99
236-TCT	98	1245-TCB	98
26 α -TCT	96	1234-TCB	99
1235-TCB	100	HCB	92
135-TBB (IS)	97	135-TBB (IS)	97
Penta	96	Lindane	91
α -BHC	94	Aldrin	91
Trifluralin	92	Octa	89
Heptachlor	91	Heptoxide	95
Oxychlor	89	Thiodan-1	95
γ -Chlordan	90	pp'-DDE	89
α -Chlordan	90	Endrin	94
Dieldrin	94	Thio-SS	95
Thiodan-2	95	pp'-DDT	89
op'-DDT	89		
Methoxy	94		
Mirex	82		

4. Hexane micro-extraction of spiked reagent water

4.1. General comments

The preparation of spiking solutions and calibration standards of OC/CB "A", OC/CB "B", PCBs, and Toxaphene was described in section 2.2 and, as outlined in section 2.3, 800 mL samples of reagent water (distilled and deionized, or HPLC grade) were each spiked with 1 mL of spiking solution. After thorough mixing, 2 mLs of hexane was added to each, and the samples were placed on the extraction rollers for at least 1 hour. Several replicates were obtained for each spiking solution.

A compilation of OC/CB "A" recovery results, representing a total of 25 replicates, are shown in Table 4.1. This includes data presented in section 3.3.1 for OC/CB "A" recoveries with 3 different volumes of hexane (extracted November 11, 1993), data resulting from the 60 minute extractions from the time study described in section 3.3.2 (extracted on November 23, 1993), and 8 other replicates extracted on July 6, 1994.

Trifluralin was added to method OWOC-E3120B target compounds some time after the onset of this project. Thus, two initial sets of data were obtained separately for this compound using TFSPK-JAN11 (see Table 2.4). In later experiments Trifluralin was included as one of the components of the OC/CB "A" spiking solution.

For the OC/CB "B" compounds, 5 experiments were conducted on January 11, 1994, 10 more on February 10, 1994, and three sets of 8 replicates on March 23, March 25, and June 14,

Table 4.1: Percent recovery for various sets of experiments of hexane micro-extractions of reagent water spiked with OC/CB "A" compounds.
(Standard deviations in parentheses)

Compound	spiked conc. (ng/L)	Percent Recovery					Combined results
		Set 1	Set 2	Set 3	Set 4	Set 5	
HCE	25	86	88 (4)	88 (2)	89 (1)	96 (3)	90 (4)
124-TCB	125	89	103 (3)	100 (1)	103 (1)	100 (2)	99 (5)
123-TCB	125	94	102 (2)	105 (1)	103 (1)	100 (1)	101 (3)
236-TCT	125	95	102 (2)	103 (1)	101 (1)	99 (1)	100 (2)
26 α -TCT	125	101	101 (1)	102 (1)	102 (1)	100 (1)	101 (1)
1235-TCB	25	94	102 (1)	103 (1)	103 (1)	101 (2)	102 (3)
PENTA	25	86	92 (2)	96 (4)	89 (2)	94 (2)	93 (4)
α -BHC	25	86	102 (1)	103 (1)	103 (1)	79 (2)	96 (11)
HEPTACHLOR	25	105	90 (5)	96 (2)	83 (4)	97 (3)	92 (7)
OXYCHLOR	50	93	90 (5)	102 (2)	88 (4)	98 (2)	95 (6)
γ -CHLORDAN	50	95	92 (5)	101 (2)	86 (4)	98 (3)	94 (7)
α -CHLORDAN	50	96	90 (5)	102 (2)	85 (4)	98 (3)	94 (7)
DIELDRIN	50	107	105 (2)	<u>109</u> (2)	102 (2)	<u>103</u> (2)	104 (3)
THIODAN-2	100	<u>108</u>	<u>106</u> (4)	102 (8)	<u>108</u> (3)	102 (3)	105 (5)
o,p'-DDT	125	102	84 (6)	99 (4)	79 (4)	96 (3)	91 (9)
METHOXY	125	102	104 (2)	106 (8)	104 (2)	<u>103</u> (2)	104 (4)
MIREX	125	98	95 (6)	103 (3)	98 (7)	85 (4)	94 (8)
TRIFLURALIN ^A	125	n/a	n/a	n/a	na/	99 (2)	92 (7)

Set 1: Nov.17,1993: 90 min. extraction, 1 mL hexane, average of duplicate experiments.

Set 2: Nov.23,1993: 90 min. extraction, 2 mL hexane, 5 reps.

Set 3: Nov.17,1993: 90 min. extraction, 3 mL hexane, 5 reps.

Set 4: Nov.23,1993: 60 min. extraction, 2 mL hexane, 5 reps.

Set 5: July 6,1994: 90 min. extraction, 2 mL hexane, 8 reps.

^ATable 4.3 lists Trifluralin results obtained prior to its inclusion in OC "A" mixture.

1994. This compilation of OC/CB "B" recovery results, representing a total of 39 replicates, are presented in Table 4.2.

The recoveries of PCB-spiked reagent water are based on 8 replicates at a spiking level of 100 ng/L, while those of toxaphene are based on 5 replicates at a spiking level of 250 ng/L. The results for PCBs, Toxaphene, and Trifluralin are listed in Table 4.3.

4.2. Analyte recovery

The results presented in Tables 4.1 through 4.3 shows that excellent recoveries can be obtained from spiked reagent water using the hexane micro-extraction technique. As explained in section 3.3 the calculated recoveries are based on internal standard quantitation relative to 1,3,5-Tribromobenzene, which was added to each sample as a surrogate standard. The combined results of 25 experiments with the OC/CB "A" compounds, conducted over an 8 month period, resulted in recoveries of at least 90% for all compounds. The highest variance in this group was observed with α -BHC. There was no one compound that consistently gave a lowest recovery (bolded) or highest recovery (underlined) within the individual sets of results for the OC/CB "A" compounds. It is notable that this extraction technique overcomes the drawback of low HCE and oxychlor recoveries, which were mentioned as limitations in the current method²³.

Five compounds of the OC/CB "B" group resulted in average recoveries of less than 90% (Table 4.2). Of these 5 compounds, only HCBd consistently had the lowest (but still acceptable) recovery within each set of experiments; the overall average recovery for this compound was 76%.

As demonstrated by the data in Table 4.3, excellent recoveries were also obtained with Trifluralin, PCBs and Toxaphene.

Table 4.2: *Percent recovery for various sets of experiments of hexane micro-extraction of reagent water spiked with OC "B" compounds.
(Standard deviations in parentheses)*

Compound	Spiked Conc. (ng/L)	Percent recovery					Combined results
		Set 1	Set 2	Set 3	Set 4	Set 5	
135-TCB	125	100 (2)	104 (6)	93 (2)	93 (1)	96 (2)	97 (5)
HCBD	25	79 (4)	75 (4)	73 (2)	69 (2)	84 (2)	76 (6)
245-TCT	125	103 (2)	105 (4)	94 (1)	95 (1)	99 (2)	99 (5)
1245-TCB	25	102 (4)	110 (4)	98 (3)	99 (3)	103 (4)	103 (6)
1234-TCB	25	106 (2)	<u>113</u> (4)	102 (2)	100 (2)	107 (2)	106 (6)
HCB	25	101 (3)	97 (5)	90 (3)	86 (1)	100 (1)	95 (6)
LINDANE	25	107 (2)	82 (6)	101 (1)	98 (1)	99 (2)	96 (9)
ALDRIN	25	92 (3)	80 (8)	79 (5)	66 (2)	95 (3)	82 (11)
HEPTOXIDE	25	110 (2)	110 (6)	104 (1)	<u>104</u> (1)	104 (1)	106 (4)
OCTA	25	86 (3)	82 (8)	81 (5)	62 (3)	93 (2)	80 (12)
THIODAN-1	50	110 (2)	105 (5)	103 (1)	103 (1)	99 (2)	104 (4)
p,p'-DDE	125	95 (4)	89 (9)	84 (6)	69 (3)	97 (3)	86 (11)
ENDRIN	100	<u>113</u> (3)	109 (6)	106 (2)	<u>104</u> (2)	<u>110</u> (2)	108 (4)
p,p'-DDD	125	106 (2)	90 (7)	95 (4)	89 (2)	105 (3)	96 (8)
THIO-SS	100	111 (3)	99 (6)	<u>110</u> (1)	101 (1)	105 (2)	104 (6)
p,p'-DDT	125	96 (4)	77 (9)	86 (7)	89 (3)	102 (4)	85 (13)

Set 1: Jan.11,1994: 60 min. ext., 2 mL hexane, 5 reps.

Set 2: Feb.10,1994: 60 min. ext., 2 mL hexane, 10 reps.

Set 3: March 23,1994: 60 min. ext., 2 mL hexane, 8 reps.

Set 4: March 25,1994: 90 min. ext., 2 mL hexane, 8 reps.

Set 5: June 14,1994: 90 min. ext., 2 mL hexane, 8 reps.

Table 4.3: *Percent recoveries of Trifluralin, PCBs and Toxaphene.
(Standard deviations in parentheses)*

Compound	Spiked conc. (ng/L)	% Recovery
TRIFLURALIN	125	91 (2) (5 reps, Jan. 12, 1994)
		85 (3) (8 reps, March 29, 1994)
		99 (2) (8 reps, July 6, 1994)
		Combined: 92 (7)
PCBs	100	103 (6) (8 reps, February 7, 1994)
TOXAPHENE	250	110 (4) (5 reps, January 12, 1994)

4.3. Comparison of recoveries: Hexane micro-extraction versus method OWOC-E3120B

Parallel recovery experiments of OC/CB "A" and OC/CB "B" compounds were conducted (June 14, 1994 and July 6, 1994, see Table 2.6) so that the performance of the current method and the proposed hexane micro-extraction method could be directly compared for recoveries from spiked reagent water, and spiked raw water. The recoveries of 8 replicates obtained by each method for spiked reagent water with OC/CB "A" and OC/CB "B" are presented in Tables 4.4 and 4.5. Quantitations by external and internal standard calculations are given for both extraction methods in Table 4.4, while in Table 4.5 the values obtained by both quantitation methods are presented only for method OWOC-E3120B. The dual presentations were necessary to facilitate a direct comparison, due to the

Table 4.4: Comparison of recoveries obtained by method OWOC-E3120B and hexane micro-extraction: HPLC water spiked with OC/CB "A" compounds (8 replicates by each method)

Compound	Spiking level (ng/L)	Percent recovery ^A			
		method OWOC-E3120B		Hexane micro-extraction	
		External standard calculation	Internal standard calculation	External standard calculation	Internal standard calculation
HCE	25	80 (6)	75 (2)	106 (5)	96 (3)
124-TCB	125	103 (10)	94 (2)	111 (5)	100 (2)
123-TCB	125	107 (9)	99 (2)	111 (5)	100 (1)
236-TCT	125	101 (8)	93 (2)	110 (4)	99 (1)
1235-TCB	25	106 (9)	96 (4)	112 (5)	101 (2)
26 α -TCT	125	114 (9)	105 (2)	111 (5)	100 (1)
PENTA	25	104 (9)	98 (3)	105 (4)	94 (2)
TRIFLURALIN	125	102 (7)	94 (3)	110 (5)	99 (2)
α -BHC	25	90 (5)	85 (2)	88 (6)	79 (3)
HEPTACHLOR	25	106 (6)	95 (3)	107 (6)	97 (3)
OXYCHLOR	50	105 (6)	98 (2)	109 (6)	98 (2)
γ -CHLORDAN	50	106 (6)	99 (2)	108 (5)	98 (3)
α -CHLORDAN	50	106 (6)	98 (3)	109 (6)	98 (3)
DIELDRIN	50	109 (7)	100 (3)	114 (6)	103 (2)
op'-DDT	125	107 (7)	98 (3)	107 (7)	96 (3)
THIODAN-2	100	107 (6)	99 (3)	114 (5)	102 (3)
MIREX	125	102 (7)	94 (5)	95 (4)	85 (4)
METHOXY	125	112 (7)	99 (4)	115 (8)	103 (3)
135-TBB (surrogate)	125	107 (8)	n/a ^B	111 (6)	n/a ^B

A. Standard deviations in parentheses.

B. Used for internal standard method of quantitation.

Table 4.5: Comparison of recoveries obtained by method OWOC-E3120B and hexane micro-extraction: HPLC water spiked with OC/CB "B" compounds (8 replicates by each method)

Compound	spiking level (ng/L)	Percent recovery ^A		
		method OWOC-E3120B		Hexane Micro-extraction
		External standard calculation	Internal standard calculation	Internal standard calculation
135-TCB	125	119 (10)	88 (3)	96 (2)
HCBD	25	89 (7)	68 (4)	84 (2)
245-TCT	125	127 (12)	96 (3)	99 (2)
1245-TCB	25	128 (14)	94 (3)	103 (4)
1234-TCB	25	145 (12)	112 (5)	107 (2)
HCB	25	134 (13)	101 (3)	100 (1)
LINDANE	25	138 (12)	103 (3)	99 (2)
ALDRIN	25	122 (13)	92 (2)	95 (3)
HEPTOXIDE	25	136 (13)	102 (2)	104 (1)
OCTA	25	117 (10)	89 (3)	93 (2)
THIODAN-1	50	130 (12)	98 (3)	99 (2)
PP'-DDE	125	125 (11)	94 (2)	97 (3)
ENDRIN	100	144 (10)	108 (2)	110 (2)
pp'-DDD	125	141 (11)	100 (2)	105 (3)
THIO-SS	100	129 (11)	96 (4)	105 (2)
pp'-DDT	125	136 (13)	98 (7)	102 (4)
135-TBB (surrogate)	125	134 (11)	100 ^B	100 ^B

A. Standard deviations in parentheses.

B. Used for internal standard method of quantitation.

differences in the magnitudes of errors and variance, as discussed in section 3.3. The current extraction method employs external standard calibration, whereas the preferred method of quantitation for the proposed hexane micro-extraction is by internal standard calculation. The recoveries had to be normalized to that of the surrogate standard in both extraction methods order to adequately compare their performance.

As mentioned in section 3.3, the use of surrogate/internal standard is useful in correcting for variations in sample preparation steps and instrumental fluctuations. This is further exemplified by the recovery data presented in Table 4.5, where recoveries of up to 145% and standard deviations of up to 14% are reported for the external standard method of quantitation. When recalculated according to the internal standard method, results improved such that the highest over-recovery dropped to 112%. Substantial improvements in precision were also observed, as indicated by the standard deviations which dropped to as low as 15% of the original value. Thus, the internal standard method of quantitation was the only meaningful way of comparing results for these methods.

According to the results shown in Table 4.4, the only significant difference observed between the two methods for the recoveries of OC/CB "A" compounds was that of HCE, for which a 20% improvement was observed with the hexane micro-extraction technique. Table 4.5, which lists the results of the OC/CB "B" recoveries, revealed another benefit in the hexane extraction method, in which the recovery of HCBP increased by approximately 15%. Thus, in addition to the advantages of speed and simplicity of this proposed method, the hexane micro-extraction technique may in some cases result in improved recoveries, most likely because of the reduction in manipulation steps prior to analysis.

4.4. Determination of MDLs, "W" and "T" values with hexane micro-extraction

According to the analytical method detection limits protocol for the municipal and industrial strategy for abatement (MISA) program, the MDL estimates are calculated as follows²⁹:

$$\text{MDL} = 3 \times \text{standard deviation} \\ (\text{based on } 8 \text{ replicates})$$

MDL determinations are conducted using clean (reagent) water samples that have been spiked with the components of interest at levels of at least 5 times and no more than 10 times the estimated MDL²⁹. Once data are acquired that meet this criterium, "W" and "T" values may also be derived from the same data, where the "W" value corresponds to the standard deviation rounded down to the nearest unit of 1, 2, or 5, and in the case of organic analytes, the "T" value equals 10 times the "W" value³⁰.

4.4.1. MDLs for OC/CB "A" compounds

A total of 13 series of spiked samples of reagent water were prepared at various concentration levels by adding 1 mL of the desired spiking solution and 1 mL of internal standard solution to 800 mL of reagent water. Thus, in all cases the internal standard (1,3,5-Tribromobenzene) concentration was 125 ng/L. Each series consisted of 8 replicate samples. After thorough mixing, 2 mL of hexane was added to each of the samples which were extracted on the rollers for 60-90 minutes. Table 4.6 lists the MDLs, "W" and "T" values determined for each OC/CB "A" component. Note that in most cases more than one value is listed. This not surprising, since MDLs are based on the absolute standard deviations, which are in turn dependent on the spiked concentrations. All the values re-

ported meet the desired criterium that the spiked concentration was 5-10 times that of the estimated MDL. By using various dilutions of the spiking solution, at least 1 MDL was determined for all components, with the exception of α -BHC and Trifluralin. The results from each series of extractions are presented in Appendix 2.

It is notable that all MDLs, "W" and "T" values determined here were as low or even lower than the current specifications³¹.

Table 4.6: MDLs, "W" and "T" values of OC/CB "A" compounds

Compound	Spiked conc. (ng/L)	Recovery (%)	Std. Dev. (ng/L)	MDL (ng/L)	W (ng/L)	T (ng/L)
HCE	0.5	96	0.02	0.06	0.02	0.2
	1	113	0.06	0.2	0.05	0.5
	1.5	116	0.07	0.2	0.05	0.5
	2.5	102	0.11	0.3	0.1	1
	5.0	72	0.17	0.5	0.1	1
	10	106	0.60	2	0.5	5
124-TCB	2.5	129	0.09	0.3	0.05	0.5
	5	116	0.20	0.6	0.2	2
	5	128	0.27	0.8	0.2	2
	10	112	0.36	1	0.2	2
123-TCB	5	114	0.22	0.7	0.2	2
	7.5	110	0.26	0.8	0.2	2
	10	104	0.34	1	0.2	2
	25	107	1.22	4	1	10
	50	103	1.83	6	1	10
236-TCT	25	94	1.14	3	1	10
26 α -TCT	2.5	109	0.11	0.3	0.1	1
	12.5	109	0.61	2	0.5	5
1235-TCB	5	99	0.2	0.6	0.2	2
	5	115	0.33	1	0.2	2

Table 4.6 (continued)

PENTA	2.5	120	0.15	0.5	0.1	1
	5	98	0.25	0.8	0.2	2
	5	107	0.22	0.7	0.2	2
	10	105	0.45	1	0.2	2
α -BHC	0.5-25	79-106	n/a	n/a	n/a	n/a
HEPTACHLOR	0.5	96	0.03	0.1	0.02	0.2
	1.5	100	0.06	0.2	0.05	0.5
	2	99	0.06	0.2	0.05	0.5
	10	83	0.36	1	0.2	2
	20	73	0.83	2	0.5	5
	25	85	1.24	4	1	10
OXYCHLOR	1	108	0.06	0.2	0.05	0.5
	3	112	0.12	0.4	0.1	1
	4	106	0.18	0.5	0.1	1
	20	84	0.74	2	0.5	5
	40	72	2.0	6	2	20
	50	90	2.4	7	2	20
γ -CHLORDAN	2	105	0.10	0.3	0.1	1
	2	106	0.12	0.4	0.1	1
	4	100	0.19	0.6	0.1	1
	20	80	0.78	2	0.5	5
	40	67	2.15	6	2	20
	50	88	2.88	9	2	20
α -CHLORDAN	2	107	0.09	0.3	0.05	0.5
	2	109	0.09	0.3	0.05	0.5
	4	102	0.21	0.6	0.2	2
	20	83	0.77	2	0.5	5
	40	71	2.1	6	2	20
	50	88	2.7	8	2	20
DIELDRIN	2	121	0.12	0.4	0.1	1
	3	121	0.17	0.5	0.1	1
	4	107	0.27	0.8	0.2	2
	40	90	2.36	7	2	20
THIODAN-2	2	116	0.08	0.2	0.05	0.5
	4	116	0.21	0.6	0.2	2
	6	122	0.22	0.7	0.2	2
	40	111	1.33	4	1	10
	40	95	1.54	5	1	10

Table 4.6 (continued)

op'-DDT	5	78	0.26	0.8	0.2	2
	5	89	0.23	0.7	0.2	2
	10	86	0.55	2	0.5	5
	50	73	2.2	7	2	20
	100	63	4.8	14	2	20
	125	82	6.7	20	5	50
	125	96	4.3	13	2	20
METHOXY	2.5	80	0.11	0.3	0.1	1
	5	88	0.18	0.5	0.1	1
	25	100	0.93	3	0.5	5
	50	97	1.9	6	1	10
MIREX	2.5	102	0.11	0.3	0.1	1
	5	106	0.20	0.6	0.2	2
	5	117	0.24	0.7	0.2	2
	50	85	2.0	6	2	20
	125	97	7.6	23	5	50
	125	85	4.4	13	2	20

4.4.2. MDLs for OC/CB "B" compounds

A total of 14 series (8 replicates each) of reagent water spiked with various concentrations of the OC/CB "B" compounds were also extracted by the hexane method. Table 4.7 lists the MDLs, "W" and "T" values that were determined. As discussed in section 4.4.1, more than 1 series of values were obtained for each compound, which depended on the spiking concentration. The results from each series of extractions are presented in Appendix 2.

With the exception of compound pp'-DDE, all the MDLs, "W" and "T" values either met or were even lower than the current specifications³¹.

4.4.3. MDL determination for PCBs

Eight 800 mL samples of reagent water were spiked with solution PCBSPKx0.4-FEB7, giving a total PCB concentration of

100 ng/L per sample. The average recovery was 103%, and the standard deviation of the 8 analyses was 6 ng/L. Thus, according to these data the estimated MDL for PCBs using the hexane roller micro extraction method is 18 ng/L, the W value is 5 ng/L and the T value is 50 ng/L. Again, these values are much lower than the current specifications³¹.

Table 4.7: MDLs, "W" and "T" values for OC/CB "B" compounds

Compound	Spiked conc. (ng/L)	Recovery (%)	Std. Dev. (ng/L)	MDL (ng/L)	W (ng/L)	T (ng/L)
135-TCB	25	100	1	3	1	10
	50	108	1.7	5	1	10
	125	104	7.1	21	5	50
HCB	3	116	0.19	0.58	0.1	1
	10	78	0.51	1.5	0.5	5
	20	82	1.25	3.8	1	10
	25	75	1.03	3.1	1	10
245-TCT	15	126	0.62	2	0.5	5
	25	110	1.2	4	1	10
	125	105	4.5	14	2	20
1245-TCB	10	109	0.34	1	0.2	2
	10	113	0.67	2	0.5	5
	20	107	0.92	3	0.5	5
	25	109	1.25	4	1	10
	25	103	1.1	3	1	10
1234-TCB	2.5	114	0.15	0.5	0.1	1
	5	107	0.20	0.6	0.2	2
	25	112	1.1	3	1	10
HCB	2.5	132	0.13	0.4	0.1	1
	3	135	0.16	0.5	0.1	1
	5	121	0.22	0.7	0.2	2
	10	106	0.44	1	0.2	2
	25	98	1.35	4	1	10

Table 4.7 (continued)

Lindane	1	113	0.045	0.1	0.02	0.2
	2	109	0.08	0.2	0.05	0.5
	2.5	110	0.10	0.3	0.1	1
	5	92	0.18	0.5	0.1	1
	5	95	0.17	0.5	0.1	1
	25	82	1.4	4	1	10
Aldrin	2.5	105	0.11	0.3	0.1	1
	5	82	0.32	1	0.2	2
	10	93	0.49	1	0.2	2
	20	82	1.03	3	1	10
	20	94	0.69	2	0.5	5
	25	79	1.33	4	1	10
Heptoxide	1	129	0.04	0.1	0.02	0.2
	2	126	0.11	0.3	0.1	1
	2.5	116	0.13	0.4	0.1	1
	10	106	0.44	1	0.2	2
	25	110	1.6	5	1	10
Octa	1	121	0.04	0.1	0.02	0.2
	2	116	0.07	0.2	0.05	0.5
	2.5	109	0.14	0.4	0.1	1
	3	118	0.1	0.3	0.1	1
	10	93	0.55	2	0.5	5
	20	79	1	3	1	10
	25	81	1.3	4	1	10
Thiodan-1	2	129	0.12	0.4	0.1	1
	20	104	1.1	3	1	10
	50	105	2.9	9	2	20
pp'-DDE	5	128	0.27	0.8	0.2	2
	10	117	0.42	1	0.2	2
	25	85	1.0	3	1	10
	50	89	1.7	5	1	10
	50	91	3.3	10	2	20
	100	84	5.0	15	5	50
	100	96	3.6	11	2	20
	125	84	8.1	24	5	50
Endrin	4	140	0.23	0.7	0.2	2
	8	124	0.31	0.9	0.2	2
	100	110	6	18	5	50
pp'-DDD	10	119	0.36	1	0.2	2
	25	95	1.4	4	1	10
	100	97	3.8	12	2	20
	100	102	3.6	11	2	20
	125	95	5.4	16	5	50

Table 4.7 (continued)

Thio-SS	8	101	0.35	1	0.2	2
	80	108	4.0	12	2	20
	100	100	5.6	17	5	50
pp'-DDT	10	92	0.4	1	0.2	2
	50	85	2.0	6	2	20
	100	84	5.6	17	5	50
	100	95	5.1	15	5	50
	125	71	4.4	13	2	20
	125	102	4.9	15	2	20

4.5. Summary

Recoveries of spiked compounds from reagent water were greater than 90% for all but five compounds, the lowest being HCBd at 76%. Direct comparison of all OC/CB analyte recoveries obtained by methods OWOC-E3120B and hexane micro-extraction revealed that hexane micro-extraction performed as well, if not better than the current method. MDLs, "W" and "T" values were determined for all but two of the target compounds with the hexane micro-extraction method. These values easily satisfy the current specifications.

5. Hexane micro-extraction of spiked real waters

5.1. General comments

Real water samples were obtained from two different water treatment facilities Ontario, one in Verner, and the other in Mississauga. Raw and treated water samples were obtained from both these locations.

Upon confirming a lack of detectable levels of the target compounds (i.e. matrix blanks), multiple samples were spiked with either OC/CB "A" or OC/CB "B" spiking solutions as described by the following:

Sixteen litres each of raw water and treated water were obtained from OCWA, Verner, thereby providing 20 x 800 mL samples of each. For both, the raw and treated water samples, 10 replicate spikes of OC/CB "A", 9 of OC/CB "B", and 1 matrix blank were each extracted with 2 mL of hexane for 90 minutes. Prior to the addition of the hexane, 100 g of NaCl was added to each sample in order to enhance recoveries by exploiting the salting out effect. These samples, particularly the raw water samples, had strong tendencies to form emulsions. This problem was easily solved by addition of about 10 drops of acetone, which was effective in breaking the emulsions such that at least 50% of the hexane extracts were recovered.

Sixteen litres of raw water was obtained from the Lakeview water treatment plant in Mississauga. Ten 800 mL samples were spiked with the OC/CB "A" compounds, and 9 samples with the OC/CB "B" compounds. One sample provided a matrix blank. This water treatment plant provides treated

water to the MOEE building; thus all Lakeview treated water samples were obtained via the laboratory tap. The tap water spikes were repeated 10 times for OC/CB "A" and OC/CB "B". All Lakeview water samples were extracted without addition of salt.

5.2. Recovery from real water samples

The average percent recovery of all compounds spiked in these real water samples are listed in Tables 5.1 and 5.2. The combined recovery results from reagent water spikes that were listed in Tables 4.1 and 4.2 are also included for purposes of comparison. All results are based on internal standard calculation relative to 1,3,5- Tribromobenzene.

In most cases excellent recoveries (>90%) were obtained from spiked raw and treated water from both sources. For some compounds, notably Mirex, Octachlorostyrene, DDTs and their metabolites, the recoveries from Verner raw water were poor, the worst case being for Mirex (26 %). The trends for some of these compounds are plotted in Figure 5.1.

It is notable that Verner raw water contains considerable levels of humics, evident from its yellow colour, and it is believed that this would account for lower recoveries of some compounds, which might have a tendency to in some way associate with the humic substances. Hence, the severity of these matrix effects had to be further investigated by comparison of recoveries by method OWOC-E3120B versus hexane micro-extraction. This also provided a more extensive basis of comparison between the two extraction methods.

An additional supply of raw water was obtained from the Verner plant, giving a total of 40 x 800 mL samples. Seventeen samples were spiked with the OC/CB "A" compounds. Nine were extracted according to the current dichloromethane extraction method, while the other eight were extracted by the hexane micro-extraction method. Matrix blanks were

Table 5.1: Percent recovery by hexane micro-extraction of compounds OC/CB "A" spiked in real water samples, compared to reagent water spikes (Standard deviations in parentheses)

compound	spiking conc. (ng/L)	% recovery				
		Verner treated	Verner raw	Lakeview treated	Lakeview raw	Reagent grade water ^A
HCE	25	93 (2)	91 (5)	106 (4)	92 (4)	90 (4)
124-TCB	125	94 (1)	102 (2)	98 (1)	96 (2)	99 (5)
123-TCB	125	99 (1)	103 (2)	96 (1)	97 (3)	101 (3)
236-TCT	125	94 (2)	95 (2)	96 (1)	95 (1)	100 (2)
1235-TCB	25	99 (1)	97 (3)	100 (2)	99 (2)	101 (1)
26 α -TCT	125	106 (3)	104 (2)	101 (1)	100 (2)	102 (3)
Penta	25	100 (4)	90 (3)	98 (5)	100 (7)	93 (4)
Trifluralin ^b	125	102 (3)	101 (3)	146 (6)	139 (5)	92 (7)
α -Bhc	25	100 (1)	101 (2)	100 (2)	99 (2)	96 (11)
Heptachlor	25	89 (2)	80 (3)	104 (2)	101 (2)	92 (7)
Oxychlor	50	106 (4)	84 (4)	104 (2)	103 (3)	95 (6)
γ -Chlordan	50	103 (1)	76 (4)	105 (2)	102 (2)	94 (7)
α -chlordan	50	102 (1)	78 (4)	104 (2)	102 (3)	94 (7)
Dieldrin	50	112 (5)	99 (3)	106 (2)	104 (3)	104 (3)
op'-DDT	125	107 (4)	57 (5)	109 (2)	103 (3)	91 (9)
Thiodan-2	100	108 (2)	103 (2)	104 (2)	101 (3)	105 (5)
Mirex	125	68 (5)	26 (3)	90 (4)	95 (5)	94 (8)
Methoxy	125	115 (8)	95 (4)	112 (3)	109 (7)	104 (4)

^AData from "Combined results" column of Table 4.1

^BThe pronounced over-recoveries from the Lakeview samples appears to have been an artifact resulting from Trifluralin instability in the instrument standard. Data are presented in Appendix 4.

Table 5.2: *Percent recovery by hexane micro-extraction of compounds OC/CB "B" spiked in real water samples, compared to reagent water spikes (Standard deviations in parentheses)*

Compound	Spiking conc. (ng/L)	Percent recovery				
		Verner treated (9 reps)	Verner raw (9 reps)	Lakeview treated (10 reps)	Lakeview raw (9 reps)	Reagent grade water ^A
135-TCB	125	87 (4)	89 (3)	96 (6)	91 (1)	97 (5)
HCB	25	57 (5)	62 (5)	76 (5)	77 (3)	76 (6)
245-TCT	125	91 (4)	92 (2)	101 (4)	94 (2)	99 (5)
1245-TCB	25	104 (3)	107 (2)	102 (5)	99 (2)	103 (6)
1234-TCB	25	106 (3)	106 (2)	104 (4)	100 (2)	106 (6)
HCB	25	118 (5)	108 (2)	108 (8)	100 (2)	95 (6)
Lindane	25	115 (2)	99 (3)	79 (7)	99 (2)	96 (9)
Aldrin	25	86 (3)	66 (2)	91 (9)	99 (4)	82 (11)
Heptoxide	25	106 (2)	99 (2)	109 (11)	108 (2)	106 (4)
Octa	25	76 (4)	48 (4)	98 (10)	94 (3)	80 (12)
Thio-1	50	104 (2)	97 (2)	107 (11)	106 (3)	104 (4)
pp'-DDE	125	92 (3)	57 (3)	113 (11)	103 (2)	86 (11)
Endrin	100	122 (3)	107 (2)	118 (13)	118 (3)	108 (4)
pp'-DDD	125	101 (4)	79 (2)	108 (11)	107 (3)	96 (8)
Thio-SS	100	97 (3)	92 (2)	106 (10)	109 (3)	104 (6)
pp'-DDT	125	102 (3)	61 (3)	109 (11)	104 (3)	85 (13)

^AData from "Combined results" column of Table 4.2

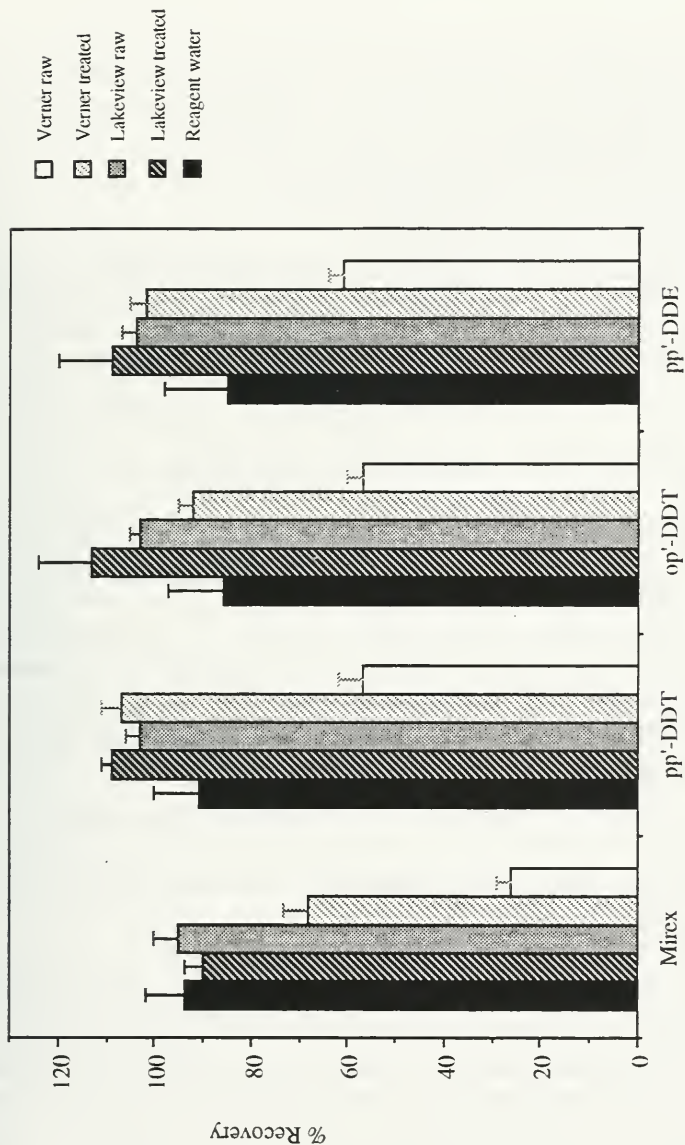


Figure 5.1: Compounds showing poor recoveries from Verner raw water

obtained using both extraction methods. Seventeen samples were also spiked with the OC/CB "B" compounds, of which nine were extracted according to method OWOC-E3120B, and eight were extracted by the hexane micro-extraction method. The recoveries that were obtained by both extraction techniques are presented in Table 5.3 and Table 5.4. For reasons already discussed in section 4.3, it is more appropriate to consider the results obtained via the internal standard method of quantitation (bolded columns of Tables 5.3 and 5.4) when comparing the two extraction procedures.

5.3. Comparison of extraction methods

According to the results shown in Table 5.3, there were no significant differences in the recoveries between both extraction methods for op'-DDT and Mirex from the spiked Verner raw water samples. In these series of experiments the samples were not salted, yet there were significant increases in recoveries for both of these compounds, compared to the results in Table 5.1. This was also observed for Aldrin, Ocachlorostyrene, pp'-DDE and pp'-DDT (Table 5.4), all of which had previously given poor recoveries from Verner raw water (Table 5.2). These differences are likely due to changes in the water, since the samples for each series were taken at least one month apart.

Overall, the data presented in Table 5.4 shows that the significant differences between the recoveries obtained by the two extraction methods are in favour of the hexane micro-extraction technique. This is better illustrated in Figure 5.2, where the recoveries of four compounds are plotted. For these compounds, increased recoveries were observed from either reagent water or unsalted Verner raw water by using the hexane micro-extraction method. For all other compounds, there were no appreciable difference in recoveries, as shown graphically in Figures 5.3 and 5.4.

Table 5.3: Comparison of extraction methods: Recoveries of OC/CB "A" compounds from Verner raw water.

Percent recovery ^A					
Compound	Spiking level (ng/L)	Method OWOC-E3120B (9 reps)		Hexane micro-extraction (8 reps)	
		External standard	Internal standard	External standard	Internal standard
HCE	25	86 (8)	93 (3)	94 (7)	95 (7)
124-TCB	125	111 (10)	94 (2)	91 (7)	96 (3)
123-TCB	125	117 (12)	100 (1)	91 (5)	96 (2)
236-TCT	125	108 (12)	93 (2)	95 (7)	99 (4)
1235-TCB	25	116 (12)	97 (3)	93 (5)	99 (3)
26 α -TCT	125	123 (14)	105 (1)	89 (5)	95 (1)
Penta	25	113 (12)	99 (1)	92 (11)	95 (7)
Trifluralin	125	101 (14)	86 (5)	93 (9)	97 (3)
α -BHC	25	100 (11)	87 (2)	68 (4)	72 (1)
Heptachlor	25	107 (12)	89 (3)	84 (6)	88 (4)
Oxychlor	50	105 (12)	89 (4)	80 (6)	85 (5)
γ -Chlordan	50	106 (13)	90 (5)	81 (6)	85 (5)
α -Chlordan	50	104 (12)	88 (4)	80 (6)	85 (5)
Dieldrin	50	109 (11)	92 (2)	87 (6)	92 (3)
op'-DDT	125	101 (12)	85 (7)	78 (7)	82 (5)
Thiodan-2	100	110 (9)	93 (3)	89 (6)	92 (3)
Mirex	125	99 (12)	84 (11)	69 (7)	74 (6)
Methoxy	125	104 (9)	86 (4)	87 (6)	91 (5)
135-TBB	125	116 (12)	100 ^B	93 (5)	100 ^B

A. Standard deviations in parentheses.

B. Used as internal standard.

Table 5.4: Comparison of extraction methods: Recoveries of OC/CB "B" compounds from Verner raw water.

Percent recovery ^A				
Compound	Spiking level (ng/L)	Method OWOC-E3120B (9 reps)		Hexane micro-extraction (8 reps)
		external standard	internal standard	internal standard
135-TCB	125	106 (8)	86 (3)	97 (3)
HCBD	25	82 (4)	67 (2)	85 (3)
245-TCT	125	124 (10)	101 (4)	97 (1)
1245-TCB	25	136 (3)	107 (7)	102 (3)
1234-TCB	25	133 (11)	110 (1)	101 (2)
HCB	25	118 (7)	96 (1)	102 (4)
LINDANE	25	129 (7)	106 (1)	83 (2)
ALDRIN	25	103 (7)	85 (1)	90 (2)
HEPTOXIDE	25	124 (7)	101 (1)	98 (2)
OCTA	25	94 (7)	77 (3)	88 (2)
THIODAN-1	50	119 (7)	97 (1)	98 (2)
pp'-DDE	125	99 (7)	80 (3)	90 (2)
ENDRIN	100	133 (9)	108 (1)	108 (2)
pp'-DDD	125	121 (7)	94 (1)	97 (6)
THIO-SS	100	120 (8)	97 (1)	92 (3)
pp'-DDT	125	91 (23)	85 (4)	94 (3)
135-TBB	125	122 (7)	100 ^B	100 ^B

A. Standard deviations in parentheses.

B. Surrogate used for internal standard calculation.

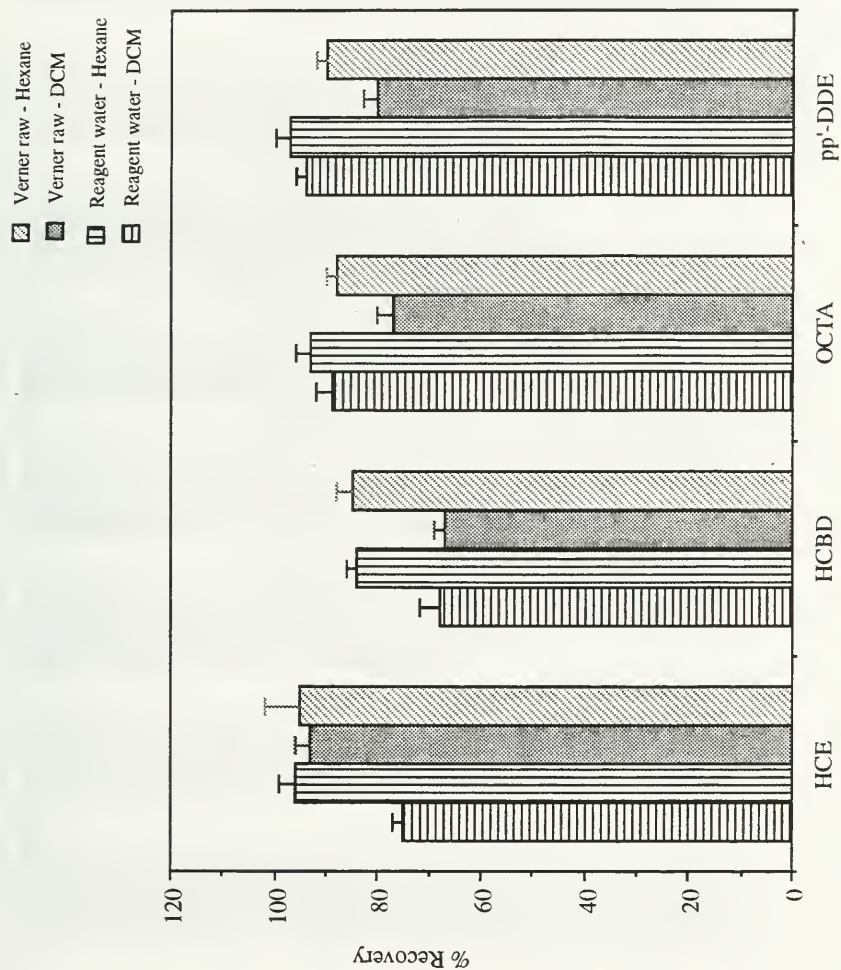


Figure 5.2: *Examples of improved recoveries by hexane micro-extraction.*

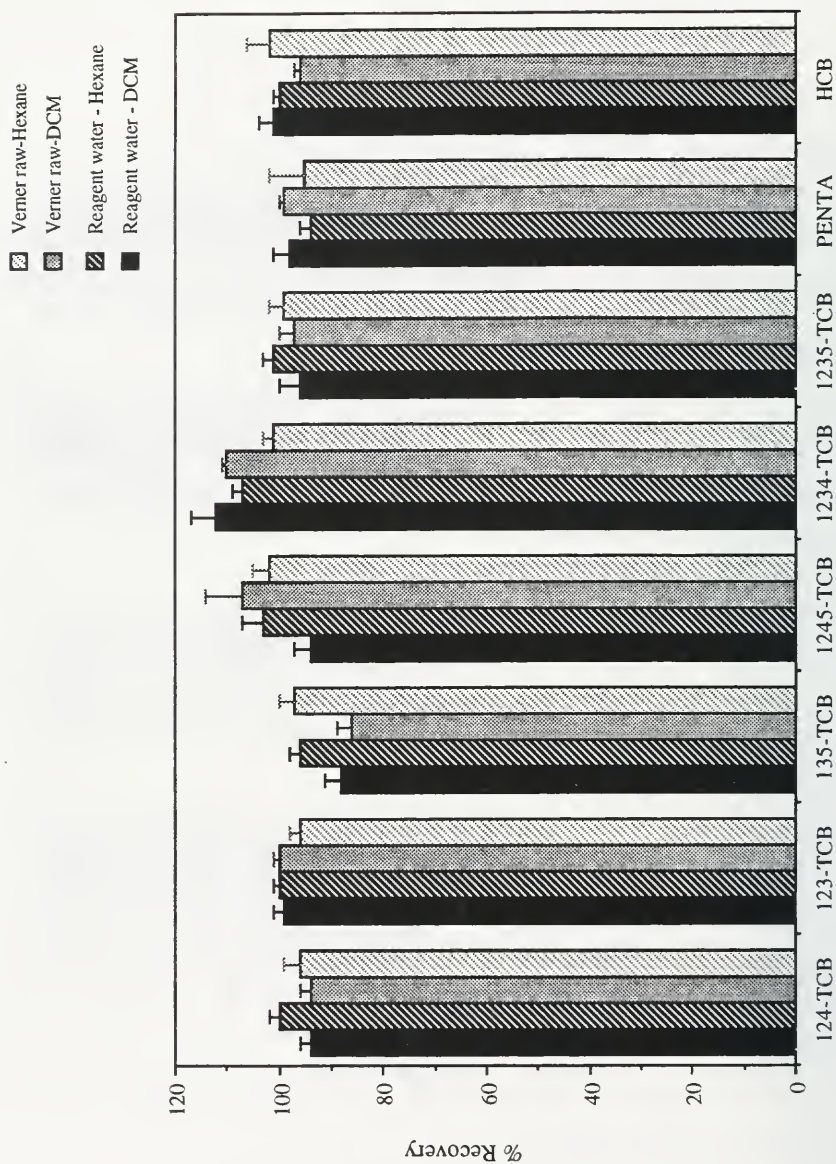


Figure 5.3: Comparisons of chlorinated benzene recoveries by both methods.

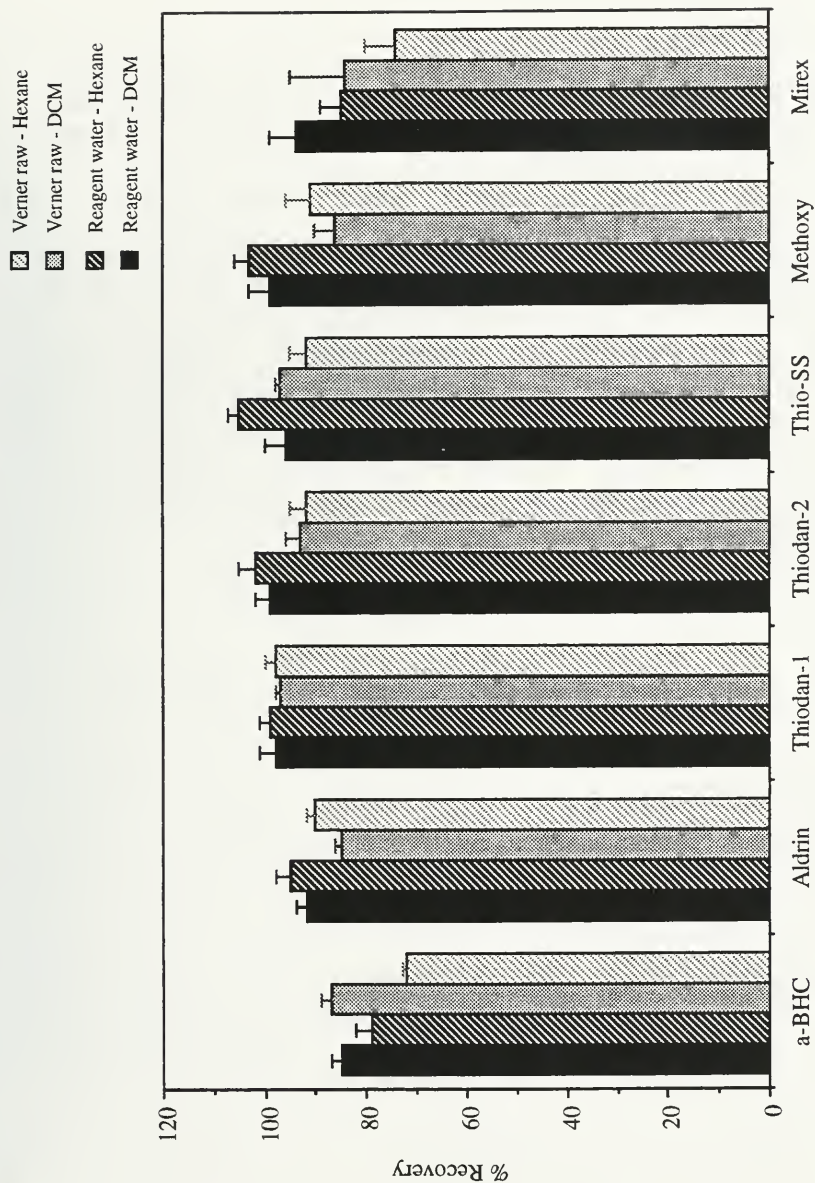


Figure 5.4: Comparison of recoveries for late eluting compounds

5.4. Summary

Data presented here demonstrated that very good recoveries could be obtained by hexane micro-extraction of OC/CB compounds spiked into real waters. The most severe cases of poor recoveries occurred with raw water obtained from the water treatment plant in Verner. These results led to further investigations, in which hexane micro-extraction and method OWOC-E3120B recoveries were directly compared for OC/CB compounds spiked into water samples from the same source. Comparing results from both methods showed that for most OC/CB compounds no significant differences in recoveries were observed. In the few cases where there was a difference, the higher recoveries were obtained by the hexane micro-extraction procedure.

6. Hexane micro-extraction of groundwater samples contaminated with PCBs and chlorinated benzene

6.1. General comments

As the final step in validation of the hexane micro-extraction method, it had to be proven on real environmental samples known to contain analytes of interest. Replicate analyses conducted on contaminated samples by method OWOC-E3120B and by the hexane micro-extraction method, and the analytical results were statistically compared.

Groundwater samples were obtained from OWCA Smithville from two different monitoring wells. This particular site was chosen because it is known to be contaminated, and considerable levels of PCBs and chlorinated benzenes have consistently been detected in water samples from this site.

6.2. Comparison by population mean values

Fourteen 1L samples were taken from each well. Each sample set was randomly divided and 7 samples were designated for analysis by method OWOC-E3120B, while the other 7 were extracted by hexane micro-extraction. The current method requires that the sample volumes be reduced to 800 mL, and normally the excess is discarded. For the purposes of this study the excess of each sample was combined to form an extra composite sample, which was extracted and analyzed by the proposed hexane method.

Table 6.1 lists the analytical results of the major compounds detected, namely PCBs, 1,2,4-Trichlorobenzene, and 1,2,3-Trichlorobenzene. The relative standard deviations obtained by both methods indicated high sample variability,

most likely because of poor sampling practice (the wells were not purged prior to sample collection), and thus a comparison of the mean values from each sample population was unsuitable for validation of the proposed method. However, it is notable that the average trichlorobenzene determination obtained from the current method was comparable to the result of the composite sample from the hexane method (bolded numbers).

Table 6.1: *Comparison of method OWOC-E3120B and hexane micro-extraction methods with real samples.*

Well #	124-TCB (ng/L)		123-TCB (ng/L)		PCBs (ng/L)	
	Hexane	OWOC-E3120B	Hexane	OWOC-E3120B	Hexane	OWOC-E3120B
34D18	72.32	12.65	28.91	5.97		
	115.00	100.12	45.47	39.19		
	13.43	109.69	8.03	42.96		
	58.62	119.01	23.75	47.83		
	121.50	26.32	48.44	10.14		
	123.68	75.78	49.27	30.47		
	92.97	17.66	37.63	8.71		
	ave:	85	34	26	nd	nd
RWS8	std. dev.:	40	15	18		
	rsd (%)	47	44	67		
	composite:	65	27			
	269.56	238.51	105.06	92.62	321.29	312.32
	265.30	262.64	102.66	101.52	364.59	380.37
	250.44	259.03	97.99	101.45	184.90	976.51
	248.41	247.85	98.42	96.92	188.96	349.17
	274.45	255.25	106.68	99.72	417.19	352.12
RWS8	263.58	245.44	102.28	98.13	378.25	504.78
	244.19	261.19	95.80	100.95	207.71	349.31
	ave:	259	101	99	295	461
	std. dev.:	12	4	3	99	236
	rsd (%)	4	4	3	33	51
	composite:	240	95		290	

6.3. Comparison by paired observations

The basis of a paired observation comparison is to determine and evaluate the confidence interval of differences observed in the determination of analytes of matched samples (pairs), each analyzed by the two different methods. Alternatively, results obtained by the proposed method can be expressed as a percent recovery based on the results obtained by the current method. Confidence intervals of the recoveries can then be evaluated. In either case the paired observation method is more useful than comparing population means when there are large variations within a population of samples.

Additional samples were obtained from the same two wells. For each set of samples (i.e. from each well) the contents of two bottles at a time were combined in a 4L bottle and shaken by hand for 30 seconds. The combined sample was then poured back into two separate bottles, and one was extracted by method OWOC-E3120B and the other by hexane micro-extraction. Results are shown in Tables 6.2 to 6.5, which also lists the 99% confidence intervals of the differences and relative recoveries..

The hexane micro-extraction method yielded satisfactory results for the analysis of chlorinated benzenes. Although according to the confidence intervals, the methods did give significantly different results, evaluation of the relative recoveries showed that on average the hexane micro-extraction recoveries were at least 90% that obtained by method OWOC-E3120B. Furthermore, the confidence intervals were very narrow, spanning only $\pm 3\%$ or $\pm 4\%$. However, this was not true for the analyses of PCBs, for which relative recoveries varied from as low as 13% to as high as 101%. In this case the average relative recovery of hexane micro-extraction was only 56%. The magnitude of the confidence interval showed that the method as is would be unacceptable for PCB analysis, not only because of the poor relative recoveries, but espe

Table 6.2: Paired determinations of 1,2,4-Trichlorobenzene (ng/L) resulting from method OWOC-E3120B and hexane micro-extraction.

Sample and Well ID	OWOC-E3120B	Hexane	relative recovery ^A (%)	Difference ^B
Well #RWS8				
pair 1	28.85	29.24	101	-0.39
pair 2	29.02	28.41	98	0.61
pair 3	27.16	26.09	96	1.07
pair 4	49.74	49.22	99	0.52
pair 5	36.01	35.18	98	0.83
pair 6	32.02	30.85	96	1.17
pair 7	170.04	168.41	99	1.63
pair 8	162.51	165.17	102	-2.66
pair 9	165.05	163.64	99	1.41
pair 10	61.96	61.00	99	0.96
pair 11	33.85	33.39	99	0.46
pair 12	26.58	25.87	97	0.71
pair 13	44.27	42.77	97	1.5
Well #29S12				
pair 1	91.09	86.12	95	4.97
pair 2	107.11	94.16	88	12.95
pair 3	101.91	92.16	90	9.75
pair 4	124.28	110.12	89	14.16
pair 5	155.20	137.75	89	17.45
pair 6	176.49	163.94	93	12.55
pair 7	138.70	124.21	90	14.49
pair 8	120.53	112.02	93	8.51
pair 9	112.11	103.33	92	8.78
pair 10	114.23	96.90	85	17.33
ave:			95	5.6
s:			5	6.4
CI ^C :			95±3	6±4
			(92->98)	(2->10)

A: relative recovery = (Hexane result/OWOC-E3120B result)x100

B: Difference = OWOC-E3120B result - Hexane result

C: CI = ave ± ts(n)^{-1/2}

Where $t_{22,0.01} = 2.83$,

s = std.dev.

n = 23 (total number of observations)

Table 6.3: Paired determinations of 1,2,3-Trichlorobenzene (ng/L) resulting from method OWOC-E3120B and hexane micro-extraction.

Sample and Well ID	OWOC-E3120B	Hexane	relative recovery ^A (%)	Difference ^B
Well #RWS8				
pair 1	17.01	17.67	104	-0.66
pair 2	16.97	16.92	100	0.05
pair 3	15.05	15.40	102	-0.35
pair 4	27.84	28.03	101	-0.19
pair 5	20.51	21.08	103	-0.57
pair 6	18.32	18.32	100	0.00
pair 7	99.64	99.23	100	0.41
pair 8	90.94	92.82	102	-1.88
pair 9	85.77	84.84	99	0.93
pair 10	33.58	32.89	98	0.69
pair 11	18.79	19.10	102	-0.31
pair 12	15.10	15.27	101	-0.17
pair 13	25.75	24.46	95	1.29
Well #29S12				
pair 1	29.66	28.08	95	1.58
pair 2	36.65	32.80	89	3.85
pair 3	33.17	30.19	91	2.98
pair 4	39.88	35.49	89	4.39
pair 5	50.42	44.89	89	5.53
pair 6	57.09	52.92	93	4.17
pair 7	45.47	39.38	87	6.09
pair 8	39.51	36.04	91	3.47
pair 9	36.42	33.32	91	3.1
pair 10	36.74	31.70	86	5.04
ave:			96	1.7
s:			6	2.3
CI ^C :			96±3	2±1
			(93->99)	(1->3)

A: relative recovery = (Hexane result/OWOC-E3120B result)×100

B: Difference = OWOC-E3120B result - Hexane result

C: CI = ave ± ts(n)^{-1/2}

Where $t_{22,0.01} = 2.83$,

s = std.dev.

n = 23 (total number of observations)

Table 6.4: Paired determinations of 1,2,3,4-Tetrachloro-benzene (ng/L) resulting from method OWOC-E3120B and hexane micro-extraction.

Sample and Well ID	OWOC-E3120B	Hexane	relative recovery ^A (%)	Difference ^B
Well RWS8				
pair 1	nd	3.86	n/a	-3.86
pair 2	4.17	3.86	93	0.31
pair 3	3.79	3.72	98	0.07
pair 4	5.61	5.24	93	0.37
pair 5	4.80	4.48	93	0.32
pair 6	4.02	3.86	96	0.16
pair 7	16.55	16.51	100	0.04
pair 8	13.43	15.63	116	-2.20
pair 9	12.12	12.09	100	0.03
pair 10	5.85	5.70	97	0.15
pair 11	4.16	4.06	98	0.10
pair 12	3.57	3.53	99	0.04
pair 13	5.03	4.85	96	0.18
well 29S12				
pair 1	1.81	1.62	90	1.12
pair 2	2.80	2.56	91	0.24
pair 3	2.15	1.92	89	0.23
pair 4	2.64	2.19	83	0.45
pair 5	2.84	2.35	83	0.49
pair 6	3.12	3.10	99	0.02
pair 7	2.22	2.05	92	0.17
pair 8	2.33	2.09	90	0.24
pair 9	2.37	2.10	89	0.27
pair 10	2.67	2.40	90	0.27
ave:			94	-0.03
s:			7	1.00
CI ^C :			94±4	-0.03±0.6
			(90->98)	(-0.6->0.57)

A: relative recovery = (Hexane result/OWOC-E3120B result)x100

B: Difference = OWOC-E3120B result - Hexane result

C: CI = ave ± ts(n)-1/2

Where $t_{22,0.01} = 2.83$,

s = std.dev.

n = 23 (total number of observations)

Table 6.5: Paired determinations of PCBs (ng/L) resulting from method OWOC-E3120B and hexane micro-extraction.

Sample and Well ID	OWOC-E3120B	Hexane	relative recovery ^A (%)	Difference ^B
Well #RWS8				
pair 1	154.30	81.52	53	72.78
pair 2	123.39	85.74	69	37.65
pair 3	104.64	88.13	84	16.51
pair 4	371.01	216.32	58	154.69
pair 5	185.65	155.48	84	30.17
pair 6	147.07	104.57	71	42.50
pair 7	752.71	670.33	89	82.38
pair 8	299.20	300.87	101	-1.67
pair 9	224.70	192.72	86	31.98
pair 10	139.10	120.31	86	18.79
pair 11	109.13	103.79	95	5.34
pair 12	106.02	91.14	86	14.88
pair 13	164.29	127.38	78	36.91
Well 29S12				
pair 1	33.99	4.58	13	29.41
pair 2	57.05	17.34	30	39.71
pair 3	34.98	5.59	16	29.39
pair 4	53.34	9.83	18	43.51
pair 5	39.35	8.24	21	31.11
pair 6	32.94	17.36	53	15.58
pair 7	53.79	8.30	15	45.49
pair 8	45.19	7.74	17	37.45
pair 9	41.73	7.60	18	34.13
pair 10	54.77	24.78	45	29.99
ave:			56	38.19
s:			31	31.47
CI ^C :			56±18	38±19
			(38->74)	(19->57)

A: relative recovery = (Hexane result/OWOC-E3120B result)x100

B: Difference = OWOC-E3120B result - Hexane result

C: CI = ave± ts(n)^{-1/2}

Where $t_{22,0.01} = 2.83$,

s = std.dev.

n = 23 (total number of observations)

cially because of the wide variability in the recoveries.

6.4. Salting samples

In a final set of experiments geared at increasing the efficiency of the hexane micro-extraction method towards PCBs by exploiting the salting out concept, another series of samples obtained from one of the monitoring wells, were prepared as described in section 6.3, and each pair was analyzed by both methods. To the samples extracted by hexane, 100 g of salt was added prior to extraction, for which the general procedure is described in section 2.3.1. The results for this series of experiments are presented in Table 6.6.

Though there was a 10% improvement in the average relative recovery, the confidence interval was still unacceptably broad, indicating high variability in the extraction efficiency.

6.5. Summary

A comparison of analytical results of Smithville groundwater samples extracted by hexane micro-extraction and method OWOC-E3120B was undertaken by paired observations. Statistical analysis of 23 pairs of results indicated only slight differences between the performances of the two methods for chlorinated benzenes. Excellent and consistent recoveries of chlorinated benzenes were obtained with hexane micro-extraction relative to that of method OWOC-E3120B, being at least 90% with narrow 99% confidence intervals of $\pm 3\%$ or $\pm 4\%$.

In contrast, rather poor results were obtained for PCBs; the relative recoveries with hexane micro-extraction were highly variable, and on average quite low ($56\% \pm 18\%$). Attempts were made to improve recoveries by salting samples prior to extraction. Somewhat higher relative recoveries

resulted, but these were still highly variable ($67\% \pm 12\%$). More research is needed to further improve his method for PCB analysis.

Table 6.6: Paired determinations of PCBs (ng/L) resulting from method OWOC-E3120B and hexane micro-extraction of salted samples.

Sample and Well ID	OWOC-E3120B	Hexane	relative recovery ^A (%)	Difference ^B
Well #RWS8				
pair 1	128.56	70.45	55	58.11
pair 2	115.03	58.72	51	56.31
pair 3	84.39	74.00	88	10.39
pair 4	126.40	75.35	60	51.05
pair 5	83.90	74.60	89	9.30
pair 6	77.00	56.88	74	20.12
pair 7	110.00	74.00	67	36.00
pair 8	118.64	70.04	59	48.60
pair 9	100.64	67.56	67	33.08
pair 10	103.74	72.30	70	31.44
pair 11	125.66	77.00	61	48.66
pair 12	149.14	70.78	47	78.36
pair 13	184.23	176.80	96	7.43
pair 14	166.57	86.13	52	80.44
ave:			67	40.66
s:			15	23.82
CI ^C :			67 $\pm$ 12 (55->79)	41 $\pm$ 19 (22->60)

A: relative recovery = (Hexane result/OWOC-E3120B result)x100

B: Difference = OWOC-E3120B result - Hexane result

C: CI = $\text{ave} \pm t_{s(n)}^{-1/2}$

Where $t_{13,0.01} = 3.02$,

s = std.dev.

n = 23 (total number of observations)

7. Preliminary experimentation with solid phase micro-extraction (SPME)

7.1. General comments

Establishing extraction parameters with SPME requires preliminary work in the following areas: Determining the required polymer coating thickness, conditions for fibre preconditioning and cleaning, required equilibration times, and optimal desorption conditions (temperature and time) that will quantitatively transfer the extracted components into the instrument, so there is no carry-over in subsequent analyses.

In this work some progress was made in these areas using solutions of HPLC grade water spiked with OC/CB "A" compounds. The fibre assembly and manual holder, fibres, sample vials and magnetic stirring equipment were all provided by J. Pawliszyn.

7.2. Fibre preconditioning

Before their use in analytical applications, all coated fibres must be preconditioned in order to rid the polymeric coating of low molecular weight oligomers and other contaminants which might produce analytical interferences. This has historically been accomplished, in a manner analagous to conditioning GC columns, by heating for several hours under inert conditions at elevated temperatures³². In this project, one fibre consisting of a 100 μm polydimethylsiloxane coating was preconditioned for 4.5 hours at 260 °C under helium in the

GC injection port, with the columns disconnected. Unfortunately, this procedure gave rise to a rather destabilized baseline, due to injector contamination, which in turn took 10 hours to return to normal. Thus, thermal conditioning of fibres is not recommended unless a "dummy injector" system is available.

More recently another method of conditioning was established, in which fibres are solvent extracted, and residual solvent is removed from the fibre by briefly heating the fibre under inert conditions³³. Another fibre that was used in this project, consisting of a 7 μm polydimethylsiloxane coating, was preconditioned by soaking in hexane for 5 minutes and desorbing at 250 °C for 5 minutes under a helium flow. This procedure was repeated twice. Figure 7.1 shows the resulting GC run, from desorption of a clean fibre after this conditioning procedure. Although not completely rid of background peaks, there was no interference with the OC/CB "A" compounds.

7.3. SPME of HPLC water and HPLC water spiked with OC/CB "A" compounds

7.3.1. Sample preparation, extraction and instrument conditions

A spiked sample was prepared by adding 1 mL of OCASPK-MAR30 to 800 mL of HPLC grade water. A 37 mL aliquot was placed in a 40 mL screw-capped vial along with a small magnetic stirring bar. The vial cap, which was tightly closed, was equipped with a teflon lined septum, which was pierced by the needle of the SPME fibre manual holder. The sample was stirred using a magnetic stirrer, at a rate just fast enough to create a 1 cm deep vortex. The coated portion of the fibre was fully suspended in the sample for 1 hour, then removed from the sample and placed in the gas chromatograph injector port for 3 minutes. The instrument conditions for analysis

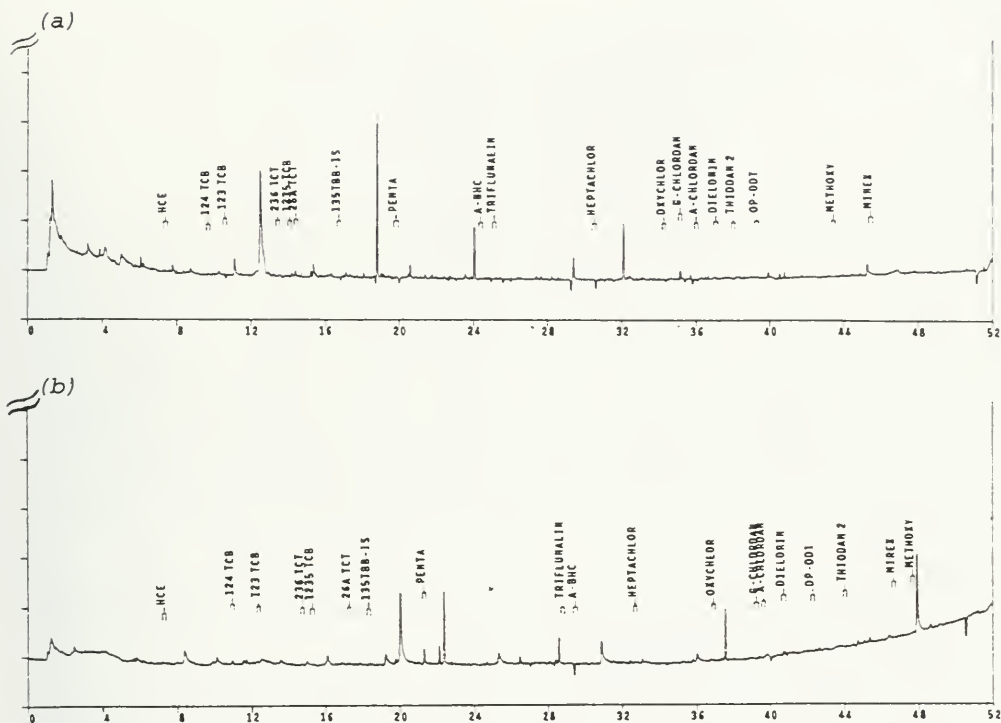


Figure 7.1: Fibre blank run after preconditioning a fibre coated with 7 μm polydimethylsiloxane.
(a) DB-1 column, (b) DB-1701 column.

were a compromise between those specified by method OWOC-E3120B, and those reported by Magdic²⁵. In this case, the injector temperature was lowered by 20 °C to prevent bleeding of the fibre coating³³. Low initial temperatures were required to allow the analytes to focus on the capillary columns after desorption from the SPME fibre. All other instrument conditions not mentioned below were kept as they were described in chapter 2.

Injector: 230 °C
Splitless mode: 0-3 min
Split mode: 3 min - endrun
Column temperature program:
Initial temp: 45 °C
Initial time: 1 min
Ramp 1: 15 °C/min
Final temp 1: 80 °C
Final time 1: 0
Ramp 2: 4 °C/min
Final temp 2: 270 °C
Final time 2: 4 min
(Total run time = 60 min)

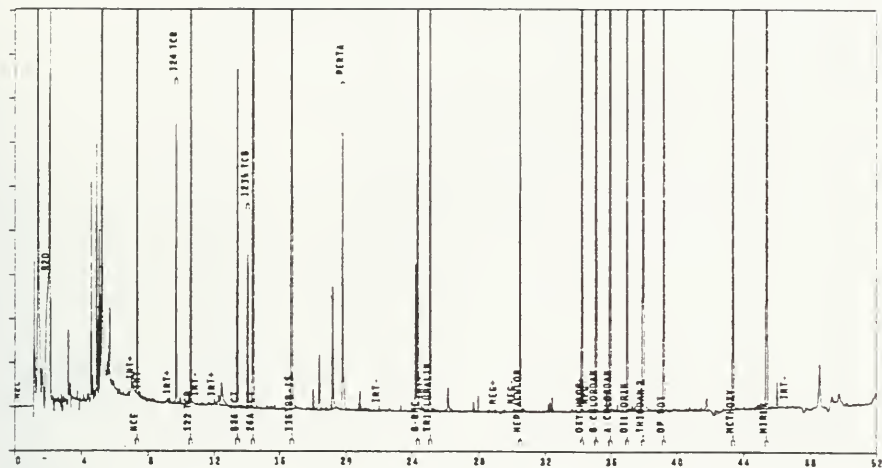
7.3.2. Results

The chromatograms shown in Figure 7.2 and 7.3 compare GC runs of the instrument calibration standard OCAINST-MAR30 against those of the SPME extraction of the spiked sample, as observed for channel 1 and 2, respectively, while Table 7.1 lists the peak areas (average of both channels) obtained for each compound from these analyses.

The concentrations of each compound present in the instrument calibration solution corresponds to that which would be obtained by 100% recovery from the entire 800 mL spiked sample in a final sample extract of 2 mL. In contrast, the SPME extraction represents a non exhaustive fibre extraction of a 37 mL aliquot of the spiked sample, yet for most of the compounds eluting after α -BHC, peak areas are considerably higher. This illustrates how method detection limits may be lowered by virtue of the fact that all analytes extracted by the fibre are transferred to the GC for analysis, rather than just a portion as with solvent extractions. However, this data also shows that for some compounds, for example α -BHC, thicker coatings, longer equilibration times, or different polymer type might be necessary to achieve detection.

In general, the SPME analysis is free of interferences in the first half of the chromatogram. In fact, the leading

(a)



(b)

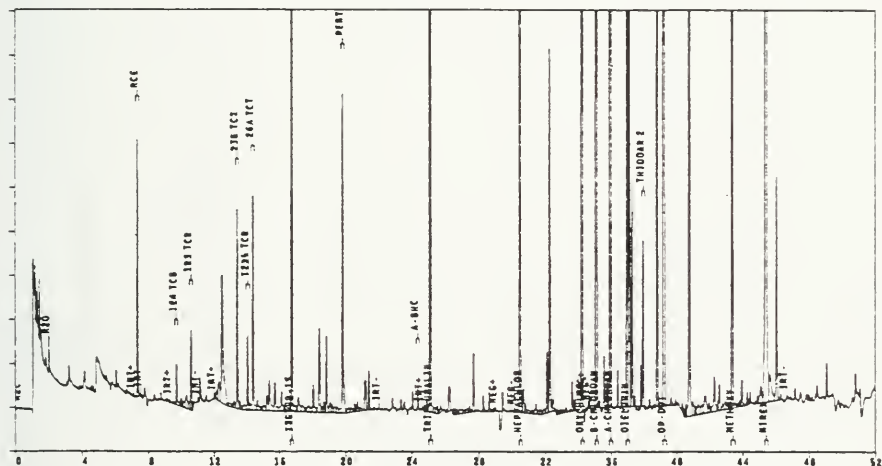


Figure 7.2: Channel 1 (DB-1) chromatograms of (a) OCAINST-MAR30 and (b) SPME of spiked HPLC water.

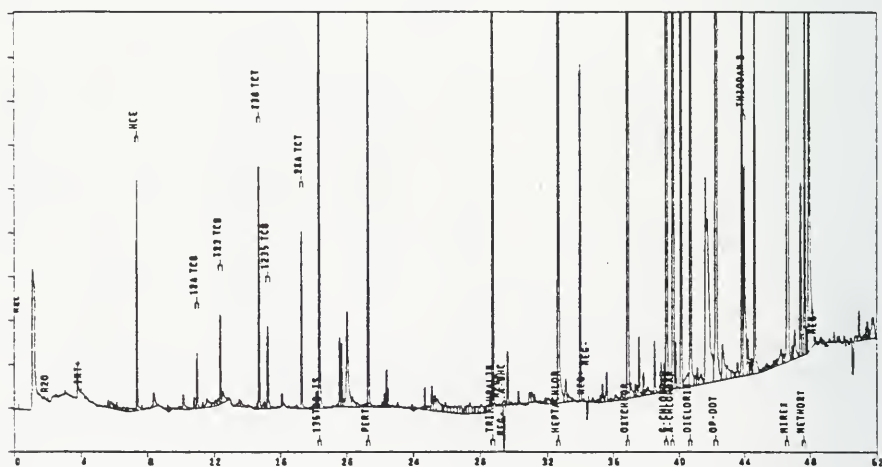
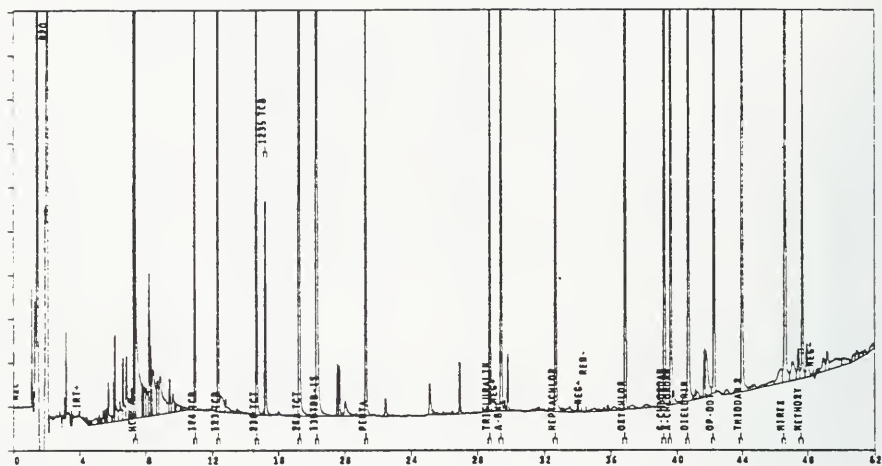


Figure 7.3: Channel 2 (DB-1701) chromatograms of (a) OCAINST-MAR30 and (b) SPME of spiked HPLC water.

Table 7.1: Comparison of peak area counts in the chromatograms of OCAINST-MAR30 and SPME of spiked HPLC water.

Compound	Area counts ($\times 10^{-4}$) (average of both channels)	
	OCAINST-MAR30	SPME of spiked HPLC water
HCE	35	7
124-TCB	13	2
123-TCB	25	3
236-TCT	18	8
26 α -TCT	85	8
1235-TCB	8	3
135-TBB (IS)	121	4
Penta	17	16
α -BHC	32	nd
Trifluralin	21	74
Heptachlor	20	105
Oxychlor	37	152
γ -Chlordan	45	214
α -Chlordan	43	185
Dieldrin	43	70
Thiodan-2	75	11
op-DDT	49	360
Methoxy	24	30
Mirex	61	447

solvent peaks present in the chromatogram of the instrument calibration solution were absent from the SPME run. However, after 29 minutes (i.e. after heptachlor), a considerable number of peaks are evident that were not present in the

instrument calibration chromatogram.

A water blank was performed prior to the analysis of the spiked sample by extracting 37 mL of HPLC grade water under the same conditions as described in section 7.3.1. The superimposed chromatograms of SPME extracted water and SPME extracted spiked water are shown in Figure 7.4. This shows that many impurities, previously undetected by liquid-liquid extraction techniques, exist in the water and are detectable by SPME. This might prove troublesome in establishing calibration standards, which consist of spiked water samples of various concentrations. Furthermore, compounds absorbed by the fibre, which coelute with target compounds, could lead to false positive results.

7.4. Optimization of injection temperature and desorption time

In the SPME technique the same fibre is used consecutively for each sample to be analyzed. Therefore, it is of utmost importance to determine the conditions required for complete desorption of all analytes from the fibre, such that there are no false positive analytical results from carry over by the fibre from one sample to the next. Following the SPME injection presented in Figures 7.2 and 7.3, the fibre was re-run under the same conditions, to determine if any residual compounds were present. The chromatograms from both channels for this experiment are shown in Figures 7.5 and 7.6. In this case, the only compound which was not completely desorbed from the fibre within 3 minutes at 230 °C was Mirex. However, in successive experiments that were conducted to establish optimal injection temperature and desorption times, oxychlor, α -chlordan, γ -chlordan, and dieldrin were also evident as residual compounds in the fibre. Of all the above, Mirex was particularly difficult to remove. Table 7.2 lists

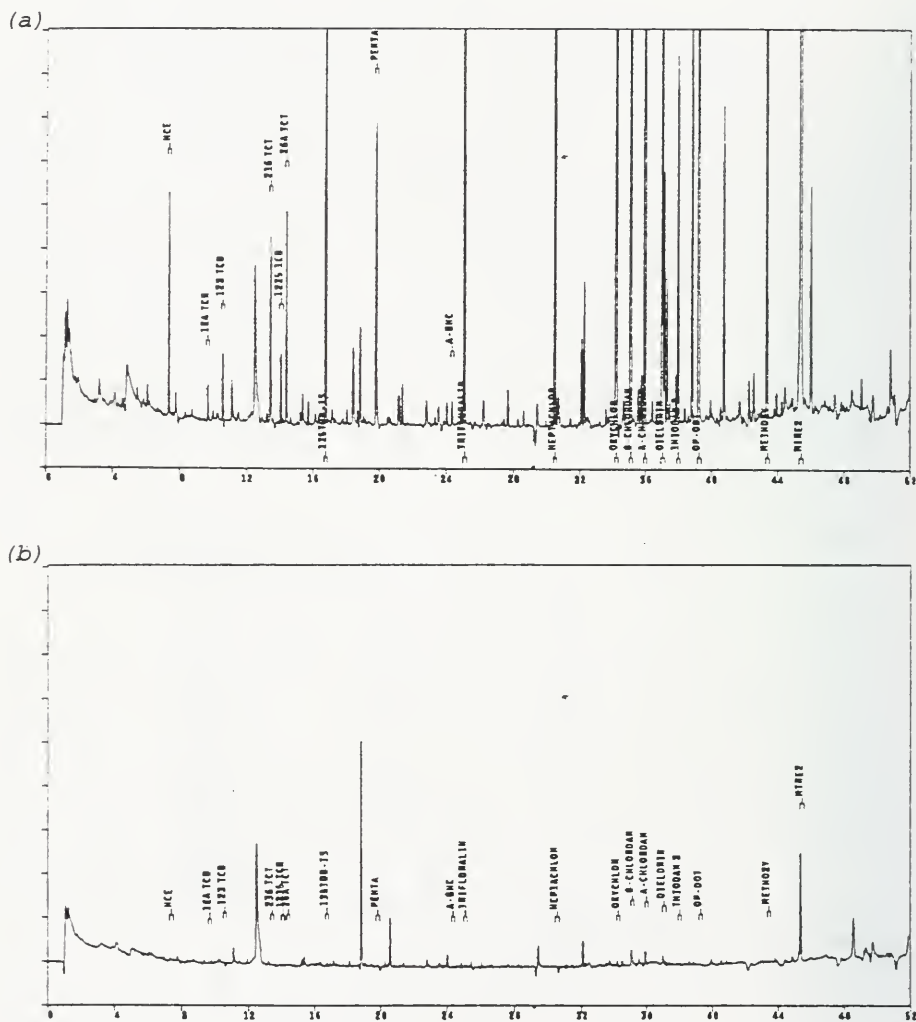


Figure 7.5: DB-1 column chromatograms of (a) SPME of water spiked with OC/CB "A" compounds, and (b) residual compounds on the fibre.

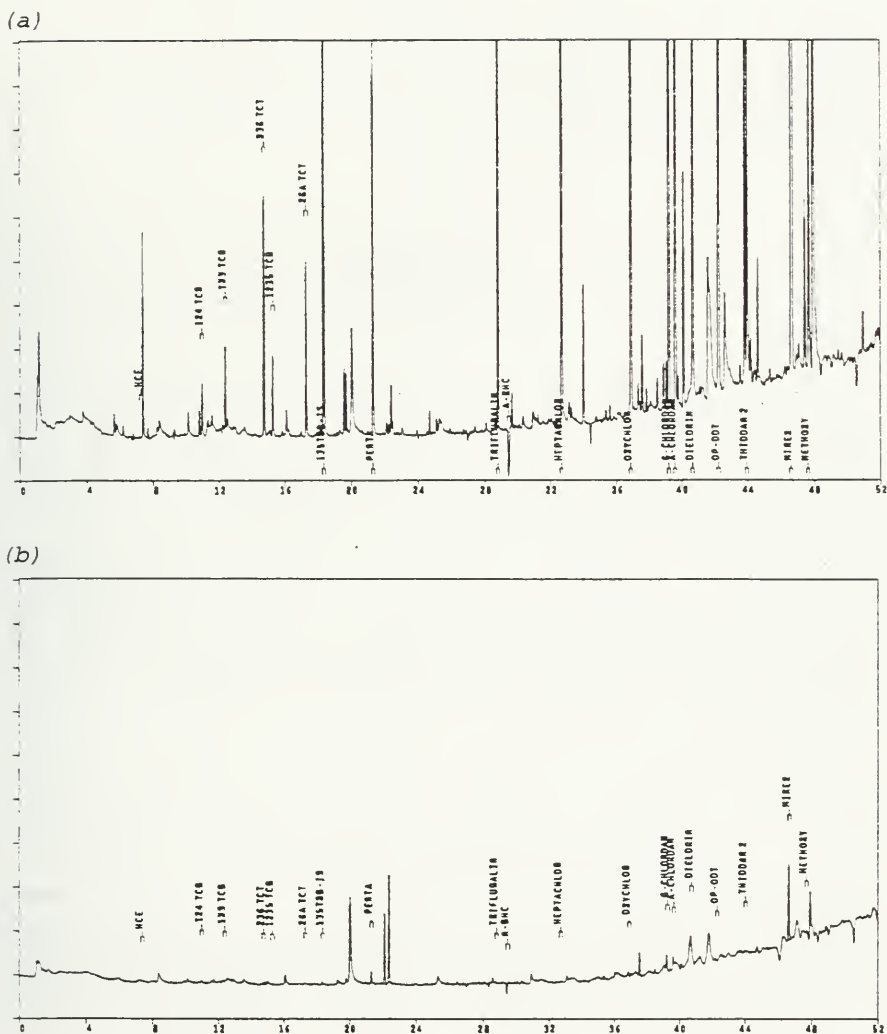


Figure 7.6: DB-1701 column chromatograms of (a) SPME of water spiked with OC/CB "A" compounds, and (b) residual compounds on the fibre.

the conditions of temperature and desorption times that were used for SPME analyses of spiked water samples. Following each run (R_A), the fibre was re-run (R_R). The relative amounts of each residual compound are given as percentages, calculated from their peak areas as follows:

$$\text{Residual (\%)} = \frac{\text{Peak Area (RR)}}{\text{Peak Area (RR + RA)}} \times 100$$

As shown from the data in Table 7.2, best results were obtained with 15 minute desorption at 250 °C. However, at this higher temperature, a lot of bleed was observed from the fibre. Notably, conditions were never established in which all of the Mirex could be removed from the fibre in one injection. It is believed that this is due to strong interaction of this compound with the glass surface of the fibre, a problem that could possibly be remedied by deactivation of the fibre prior to applying the polymer coating³⁴.

Table 7.2: *Desorption conditions and measured percent residual compounds carried over.*

Desorption conditions	Residual (%)				
	Oxychlor	γ -Chlordan	α -Chlordan	Dieldrin	Mirex
230 °C; 3 min	nd	0.75	0.56	nd	1.2
230 °C; 4.5 min	0.3	0.61	0.41	2.2	1.9
230 °C; 30 min	0.65	1.2	1.0	1.0	2.6
250 °C; 3.5 min	nd	nd	nd	4.8	1.0
250 °C; 6 min	0.2	0.3	0.2	1.1	1.0
250 °C; 15 min	nd	nd	nd	nd	0.44

7.5. Equilibration time

Determination of the time required for all compounds to achieve equilibrium between the aqueous and polymer phases is key in obtaining reproducibility and in maximizing detectability.

Equilibration time is determined by plotting detector response as a function of extraction time. In this case desorption conditions of 230 °C for 30 minutes (with injector in splitless mode for 6 minutes) were chosen. Under these conditions fibre bleed and Mirex carry-over were minimal. However, this meant that in order for the analysis as a whole to be efficient (desorption and subsequent extraction complete within the total GC run time of 60 minutes), equilibration had to be demonstrated within 30 minutes.

Aliquots of an HPLC water sample spiked with OC/CB "A" compounds were extracted by SPME for 1, 5, 15 and 30 minutes. The time profiles for all compounds, shown in Figure 7.7, indicate that equilibration is achieved within 15-30 minutes for all compounds with GC retention times of less than 20 minutes. However, for the other compounds the time profiles indicate a more complex and lengthy process in partitioning between the aqueous and polymer phases: A sudden increase was observed at 30 minutes, after initially leveling out within 15 minutes. This is attributed to initial sorption of compounds to the glass walls of the vial, which after some time also partition into the aqueous and polymer phases. Deactivation of the glass surfaces of the vials has been effective in minimizing this effect and shortening equilibration times³⁴.

7.6. Summary

Preliminary experiments were conducted on HPLC grade water spiked with OC/CB "A" compounds, geared at establishing SPME extraction parameters. Evidence of superior attainable

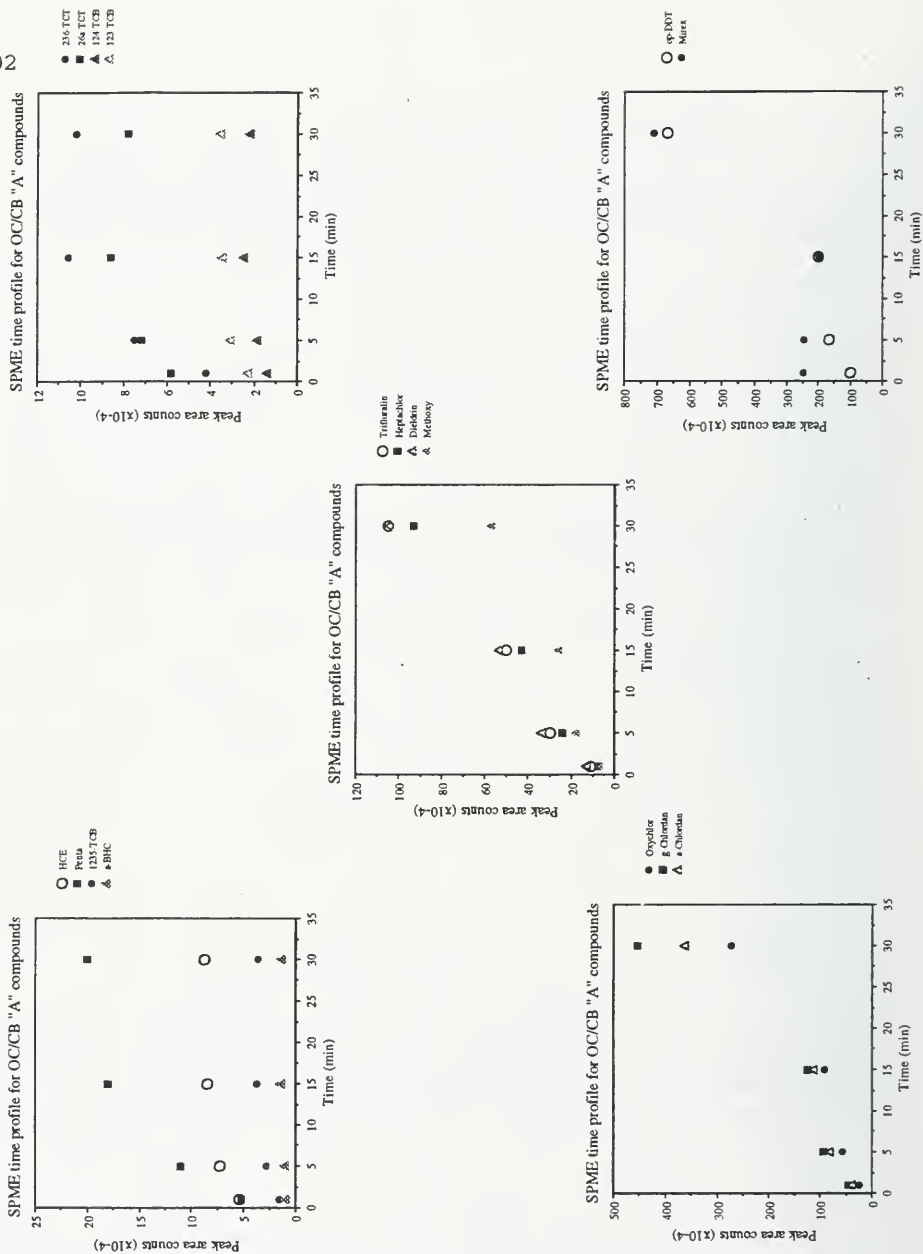


Figure 7.7: SPME time profiles for OC/CB "A" compounds: Peak areas (average of both channels) versus time of extraction.

detection limits were observed, in that large detector responses were obtained for many compounds from a relatively small aliquot of spiked water. However, this was not the case for all compounds making up the OC/CB "A" mixture. Notably, α -BHC was difficult to detect with this method, under the conditions used. Detection of all compounds can be enhanced by increasing the film thickness and extraction time, but in order to optimize the analysis in terms of sample throughput, the combined extraction and desorption time should not exceed that of the GC analysis time.

Difficulties were encountered in fully removing all compounds from the fibre during the desorption step. Evidence of Mirex carry-over was present even after desorption times of 15 minutes at 250°C, which is the maximum recommended operating temperature for the injector. Though these conditions did yield the best results in terms of minimizing carry-over, a higher background from fibre bleed was observed. A combination of deactivation of the fibre surface prior to coating with the polymer, followed by more thorough means of preconditioning the polymer film should resolve these problems.

Some experiments were conducted to determine equilibration times. However, these were limited to a maximum extraction time of 30 minutes, due to considerations of GC run time and desorption times, as mentioned above. Only in a few cases was equilibration evident within this time frame. For most of the compounds, those with retention times greater than 20 minutes, there was a significant increase in response at the 30 minute time point. More information is needed to determine the equilibration times of these compounds. It is expected that deactivation of the glass surfaces within the sample vials would lessen equilibration times.

8. Conclusions and recommendations

8.1. Hexane micro-liquid-liquid extraction

Based on the results of this project, hexane micro-extraction appears to be a viable alternative to the liquid-liquid extraction specified in method OWOC-E3120B, although more work is required to improve the extraction efficiency for PCB analysis.

Excellent recoveries were obtained for most target analytes from spiked reagent and real waters, and hexane micro-extraction tended to offer a higher degree of accuracy and precision compared to the current method. Furthermore, experiments to determine MDLs indicated that hexane micro-extraction could easily meet the current specified detection limits.

In the analysis of real samples, hexane micro-extraction yielded only slightly lower recoveries of chlorinated benzenes compared with the current method. These results were very consistent. Benefits of reduction in solvent use, simplicity and speed of analysis, all justify accepting this method despite the slightly lower recoveries.

Unfortunately, PCBs also present in these samples were not successfully extracted using the hexane method. Poor and highly variable recoveries were obtained compared to the current method. Admittedly, fewer experiments with PCBs were performed during the course of this project. Only recovery experiments from reagent water were conducted, for the purpose of determining MDL values. This was also the case for Toxaphene. Thus, more work is required to develop this method for these two classes of compound.

In contrast, extensive experimentation was conducted with chlorinated benzenes, as they are included in the OC/CB mixtures. Over all, the relative recoveries of these compounds from the Smithville samples corresponded very well to those seen in recovery experiments from spiked reagent and real waters. This supports the use of hexane micro-extraction for the determination of OC/CB in real waters as an alternative to the current extraction method.

It is likely that only minor variations are required to improve the extraction efficiency of this method for PCB analysis. It is recommended that the following two parameters be explored to further optimize the hexane micro-extraction method:

(1) Increasing the amount of salt:

EPA method 505, which includes the analysis of PCBs using this extraction procedure, specifies the addition of 6g NaCl to 35 mL samples. This corresponds to approximately 140g NaCl for each 800 mL sample. In this work, a maximum of 100g NaCl was added to the samples in salting experiments, which was perhaps deficient. Alternatively, addition of Na_2SO_4 might be more effective in raising the ionic strength of the solution.

(2) Increasing the volume of hexane:

In chapter 3 it was demonstrated that the extraction efficiencies using 2 mL hexane was above 90% for most compounds. However, some compounds such as Mirex were more difficult to extract. According to the equations presented in chapter 1, decreasing the water-to-organic phase ratio should improve extraction efficiency. Thus, increasing the hexane volume to improve PCB recovery is recommended. In EPA method 505, 35 mL of water is extracted with 2 mL hexane, resulting in water-to-organic phase ratio of 17.5. For the experiments

conducted throughout this project, this phase ratio was 400. Using hexane volumes of 5-10 mL would lower the phase ratio to 80 or 160, which can yield a significant difference in extraction efficiency. However, larger hexane volumes might raise detection limits and/or complicate the method by the addition of a concentration step. A suitable compromise will have to be found in this respect.

8.2. Solid phase micro-extraction

The most striking features observed in the preliminary SPME experimentation were the impressive detector responses obtained for many compounds after extraction of a relatively small aliquot of water spiked with the OC/CB "A" mixture, and the simplicity by which this was achieved. Notably, α -BHC was barely detectable under these conditions, but increasing the film thickness can remedy this situation. However, in general one is limited in increasing film thickness, because thicker films require longer equilibration times, and longer desorption times. Furthermore, they are more difficult to precondition.

In this work two approaches were taken in fibre preconditioning: Thermal treatment, and solvent washing of the polymer film. In either case, a dummy injector system is recommended in future work, to avoid contamination of GC systems, and to allow for more aggressive thermal treatments. In this work, a total baseline was not achieved after preconditioning, but none of the peaks observed from the fibre interfered with the compounds of the OC/CB "A" mixture. However, if one considers all target compounds, difficulties might be encountered. More aggressive fibre pretreatment should be undertaken in future work, for example thermal treatment at 320 °C for 2 hours³⁴.

Problems were encountered with the carry-over of certain

compounds after the SPME procedure. Mirex was particularly difficult to remove from the fibre. This is attributed to its sorption to the glass surface of the fibre, rather than affinity to the polymer coating. Using treatments similar to that of the production of wall coated fused silica capillary columns, the deactivation of fibre surfaces should be conducted prior to coating with the polymer film.

In this project, due to problems encountered with carry-over and fibre bleed, a relatively low desorption temperature (230 °C) was used in conjunction with a rather long desorption time (30 minutes). In order to optimize the analysis as a whole, (i.e. for sequential analyses to be conducted within one GC run time), equilibration of all compounds between the aqueous and polymer phase had to be attained within 30 minutes. This was only demonstrated for 8 of the compounds in the OC/CB "A" mixture. It is believed that the excessive equilibration times observed for the other compounds of this mixture was the result of their initial sorption to the glass surfaces of the sample vials, and the rate-limiting subsequent partitioning between the solid and liquid phases³⁴. Faster equilibration is expected with deactivated sample vials.

In summary, much more work is needed in order to assess the viability of SPME as a technique for the determination of organochlorine pesticides in water. The following approach is recommended for future work:

- (1) **Deactivated fibres, with thin polymer films that are thoroughly preconditioned.**

To eliminate carry-over and minimize desorption times.

- (2) **Deactivated glass surfaces of the sample vials:**

To minimize equilibration times of all target compounds.

(3) Reassessment of equilibration times:

Ideally, for purposes of maximum sample throughput, this should be within 1 hour (GC analysis time) less the desorption time.

(4) Determination of method detection limits:

Demonstrate that the method meets current specifications for all compounds.

(5) Compare SPME performance to existing method with real samples.

It is notable that from the standpoint of sample throughput, SPME can only out-perform hexane micro-extraction if an automated SPME system can be implemented, and even then, only if the combined extraction and desorption times are within that required for GC analysis. With manual SPME procedures, at most 8 injections can be performed within one workday. In contrast, with hexane micro-extractions many samples can be concurrently prepared for analysis, and with the use of the autosampler up to 20 samples can be analyzed within a 24 hour period.

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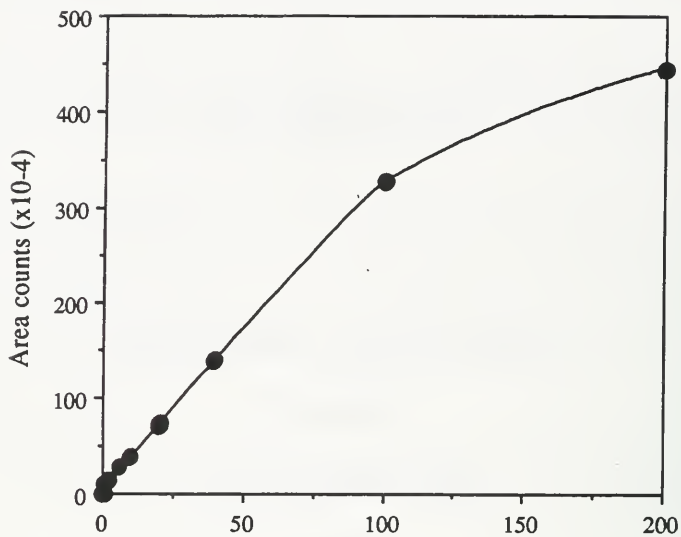
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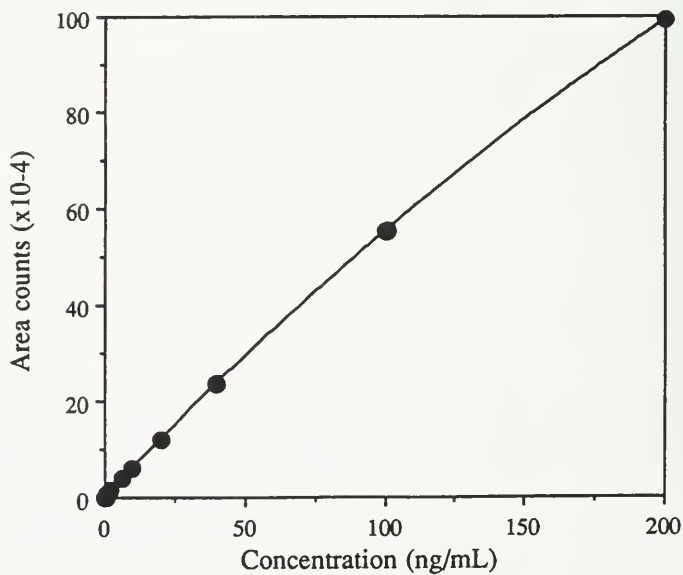
APPENDIX 1:

**DETECTOR RESPONSE
VERSUS
CONCENTRATION
FOR
OC/CB "A" COMPOUNDS**

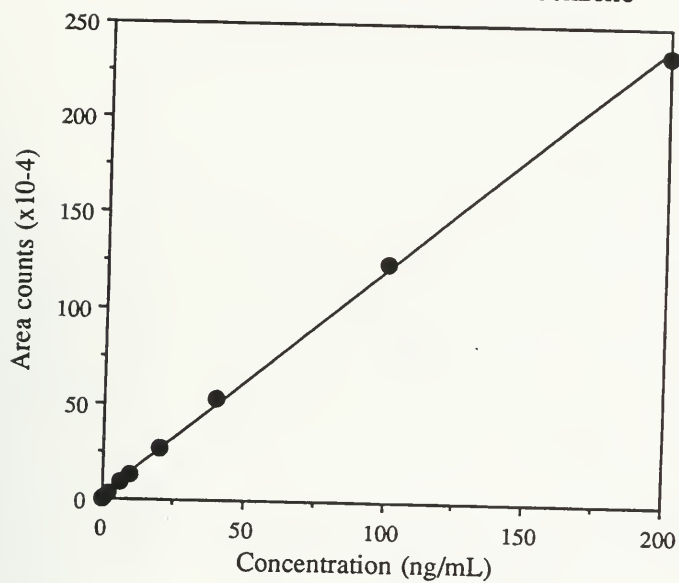
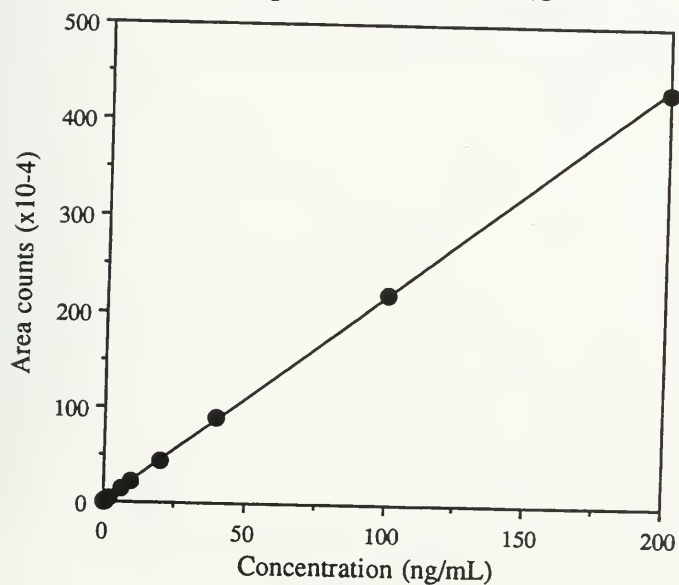
Response curve for Hexachloroethane



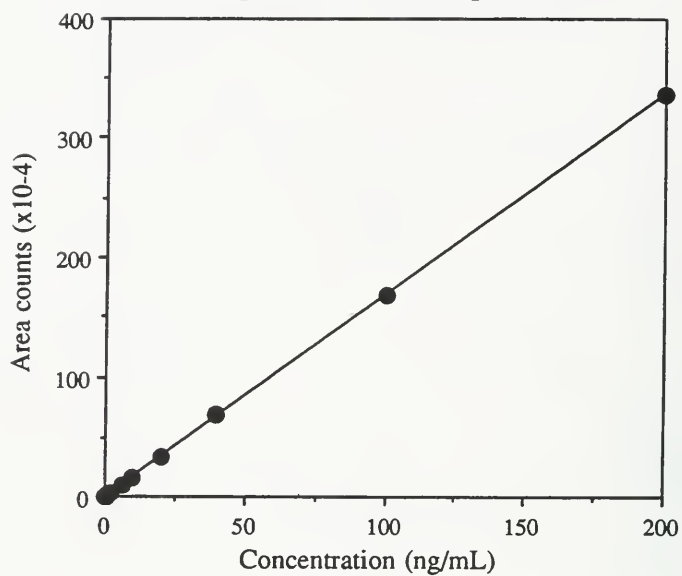
Response curve for 1,2,3,5-Tetrachlorobenzene



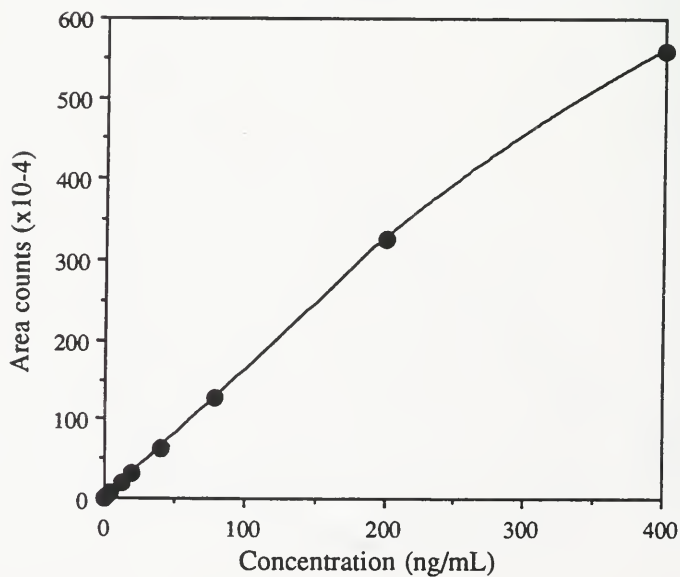
Response curve for Pentachlorobenzene

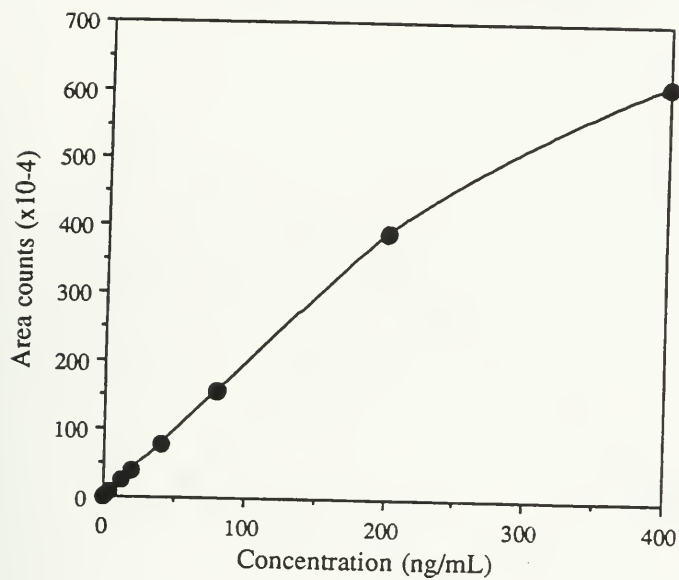
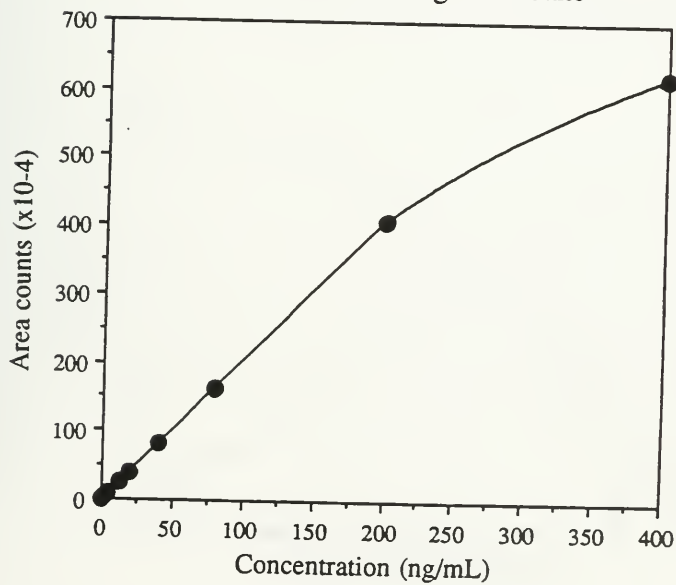
Response curve for α -BHC

Response curve for Heptachlor

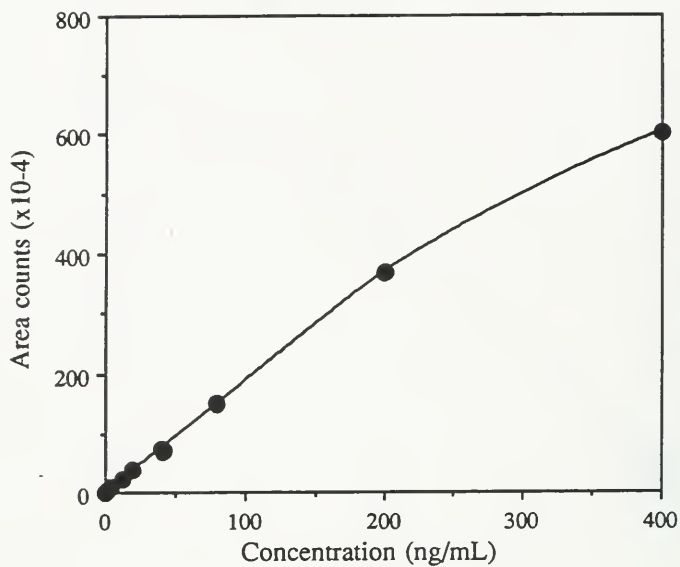


Response curve for Oxychlor

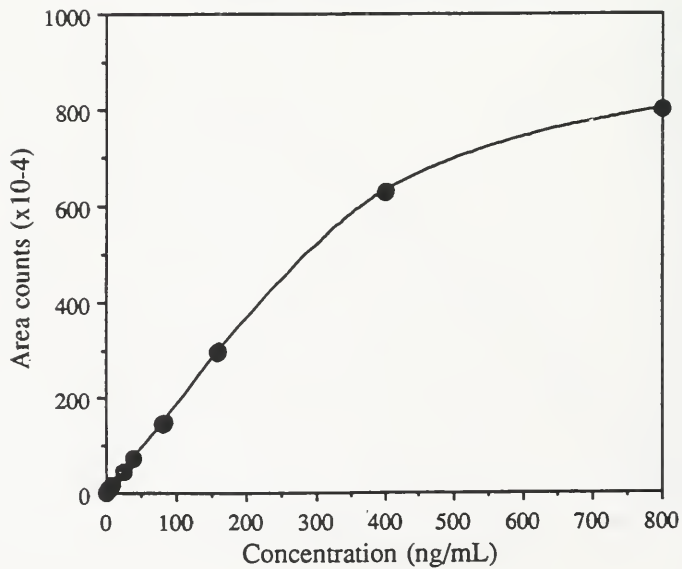


Response curve for α -ChlordaneResponse curve for γ -Chlordane

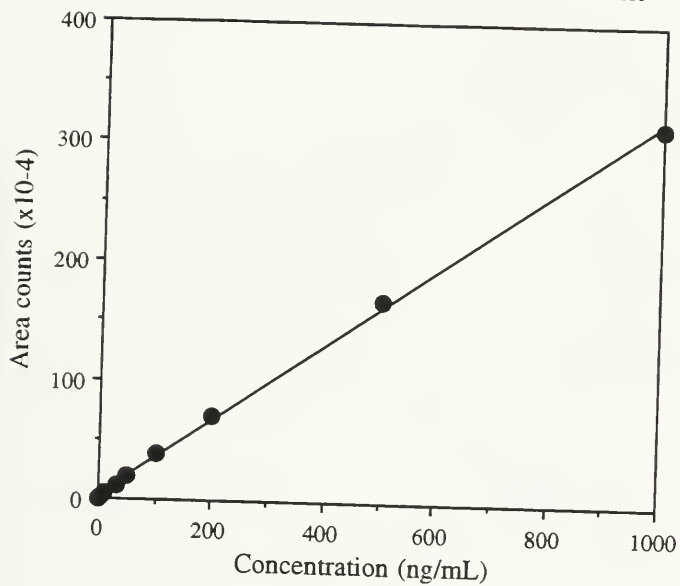
Response curve for Dieldrin



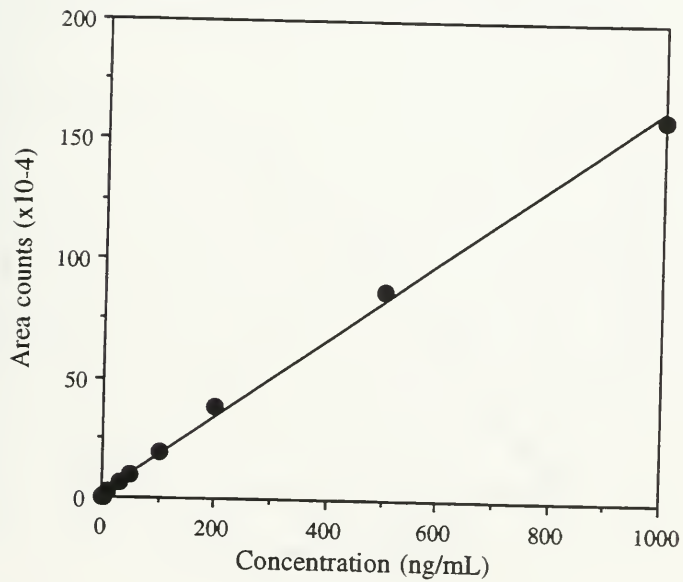
Response curve for Thiodan-2



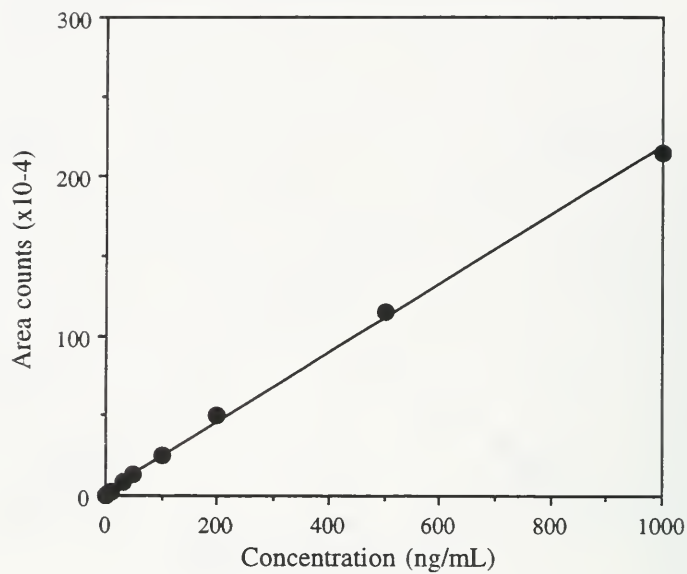
Response curve for 1,2,3-Trichlorobenzene



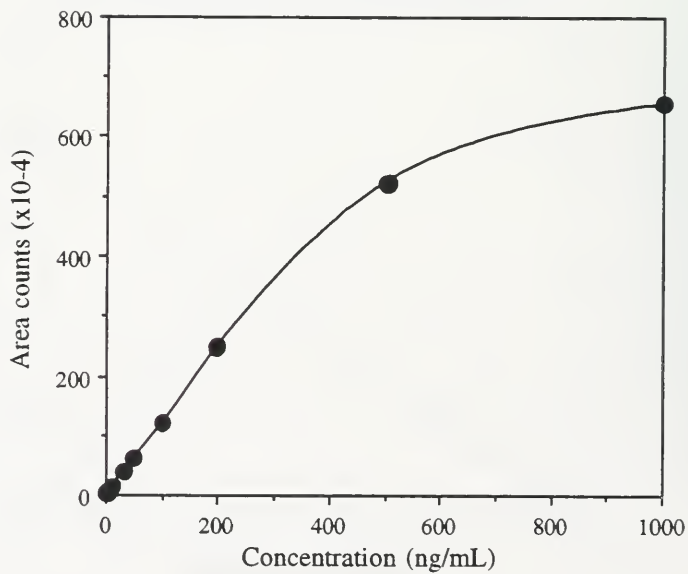
Response curve for 1,2,4-Trichlorobenzene



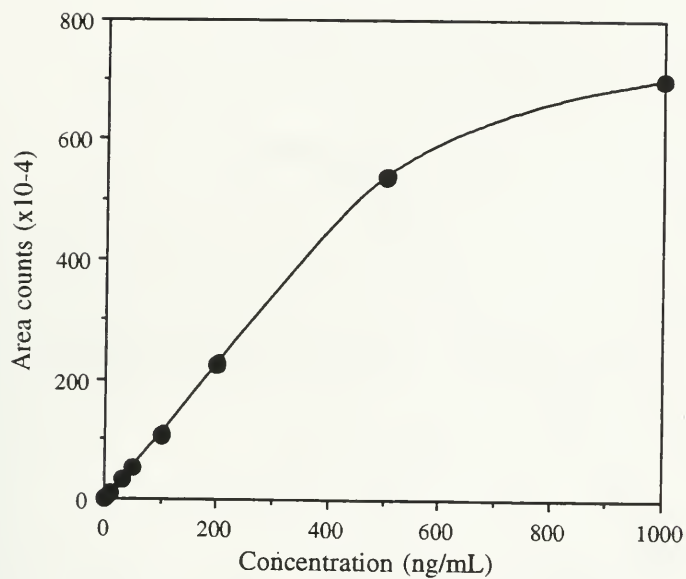
Response curve for 2,3,6-Trichlorotoluene



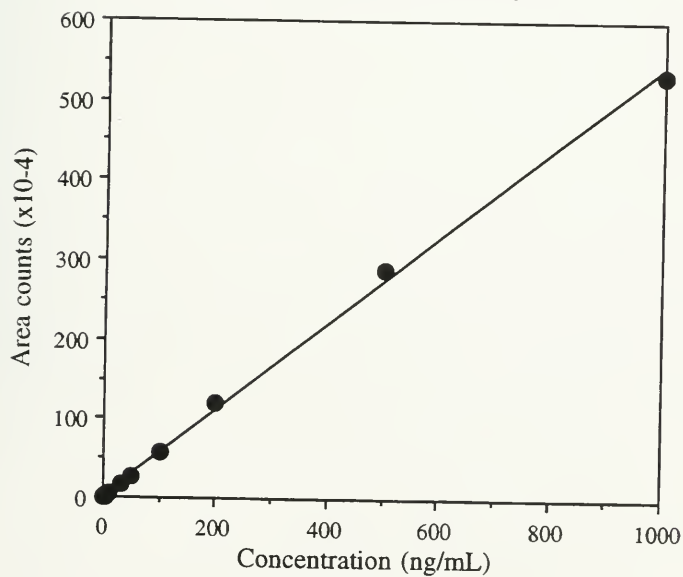
Response curve for 2,6,a-Trichlorotoluene

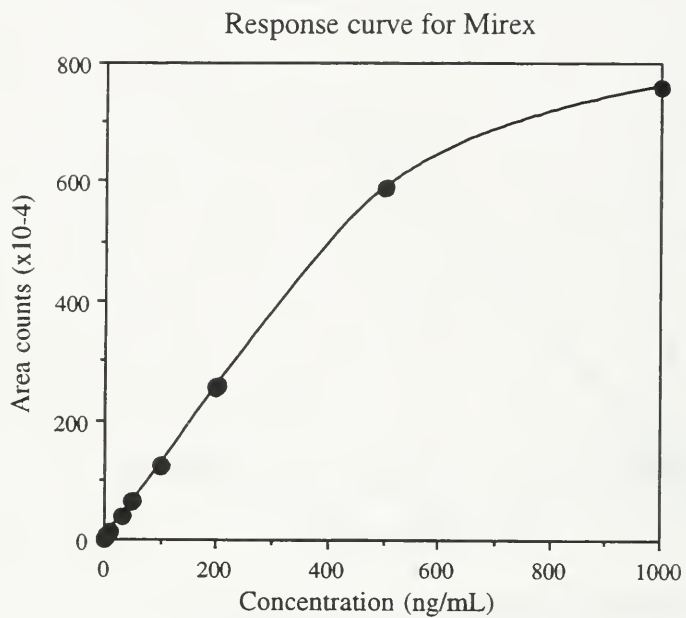


Response curve for o,p'-DDT



Response curve for Methoxychlor





APPENDIX 2:

REPLICATE SPIKE RECOVERIES
FOR THE
DETERMINATION OF
MDLs, "W" AND "T" VALUES

November 23, 1993

Determination of MDL values for OC/CB "A" compounds. Normal spiking levels.

126

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	25	21.94	22.16	22.44	21.99	22.51	20.54	22.29	21.97	21.98	88	0.62	1.86	No
124-TCB	125	129.08	128.37	128.83	128.09	129.38	123.77	129.21	131.81	128.57	103	2.24	6.70	No
123-TCB	125	128.62	128.39	129.18	126.43	127.45	124.81	127.73	129.79	127.80	102	1.60	4.80	No
236-TCT	125	126.18	127.46	126.80	126.56	127.48	124.02	127.63	127.51	126.70	101	1.21	3.63	No
1235-TCB	25	25.74	25.99	25.36	25.71	25.50	25.54	25.73	25.68	25.66	103	0.19	0.57	No
26 α -TCT	125	127.69	126.50	127.18	125.43	125.68	124.90	125.11	127.12	126.20	101	1.06	3.18	No
PENTA	25	22.30	22.81	22.03	22.56	23.06	23.58	23.12	22.49	22.74	91	0.50	1.50	No
α -BHC	25	26.08	25.56	25.89	25.60	25.49	25.90	25.66	25.82	25.75	103	0.20	0.60	No
HEPTACHLOR	25	22.12	19.54	20.29	21.42	23.36	20.70	22.21	20.63	21.28	85	1.24	3.72	Yes
OXYCHLOR	50	46.05	41.51	43.20	45.63	49.36	43.77	46.76	44.09	45.05	90	2.43	7.29	Yes
γ -CHLORDAN	50	45.33	40.51	41.56	44.45	49.44	43.26	46.39	42.51	44.18	88	2.88	8.64	Yes
α -CHLORDAN	50	44.88	39.73	41.41	44.59	48.29	43.15	46.29	43.29	43.95	88	2.70	8.10	Yes
DIELDRIN	50	51.45	49.44	50.68	51.56	51.31	51.32	53.88	51.99	51.45	103	1.25	3.75	No
op'-DDT	125	106.46	97.56	94.34	100.78	114.93	104.77	106.98	97.42	103.91	82	6.70	20.10	Yes
THIODAN-2	100	109.46	107.62	109.12	104.39	102.42	105.07	109.75	109.41	107.16	107	2.82	8.46	No
MIREX	125	110.69	131.19	119.04	129.31	117.98	117.83	130.84	117.18	121.76	97	7.64	22.90	Yes
METHOXY	125	128.83	128.30	127.93	133.58	127.63	131.64	132.53	128.96	129.92	104	2.30	6.90	No

February 2, 1994
Determination of MDL values for OC/CB "B" compounds. Spiked at 0.2 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	25	24.46	24.75	25.38	24.00	25.25	27.34	24.75	24.25	25.02	100	1.04	3.12	Yes
HCB	5	3.60	3.50	3.56	3.38	3.56	3.60	3.44	3.13	3.47	69	0.16	0.48	No
245-TCT	25	23.54	27.06	29.13	26.31	24.94	25.81	24.05	25.00	25.73	103	1.79	5.37	No
1245-TCB	5	4.30	5.88	5.75	5.50	5.38	5.33	5.38	5.13	5.33	107	0.52	1.56	No
CYCLOPENT	10	10.50	10.75	11.25	10.63	10.25	10.63	10.00	9.50	10.44	104	0.53	1.59	Yes
1234-TCB	5	4.79	5.88	5.31	5.75	5.63	6.03	5.56	5.44	5.55	111	0.39	1.17	No
HCB	5	5.21	5.31	5.25	5.00	5.38	6.46	5.13	5.13	5.36	107	0.46	1.38	No
LINDANE	5	4.56	4.56	5.00	4.56	4.56	4.75	4.50	4.44	4.62	92	0.18	0.54	Yes
ALDRIN	5	4.43	4.25	4.00	3.93	4.25	4.63	3.69	3.81	4.12	82	0.32	0.96	Yes
HEPTOXIDE	5	5.49	5.44	5.63	5.25	5.56	6.99	5.44	5.31	5.63	113	0.56	1.68	No
OCTA	5	4.26	4.19	4.56	3.75	4.25	4.88	4.00	3.50	4.17	83	0.44	1.32	No
THIODAN-1	10	10.61	10.38	10.50	9.94	10.50	12.25	10.25	9.75	10.52	105	0.76	2.28	No
pp'-DDE	25	22.36	21.00	21.50	19.88	21.88	22.50	20.81	20.00	21.24	85	1.00	3.00	Yes
ENDRIN	20	22.01	21.56	21.88	20.63	21.38	26.38	21.31	21.06	22.03	110	1.81	5.43	No
pp'-DDD	25	24.06	23.63	23.31	22.69	23.63	26.50	22.81	21.81	23.56	95	1.38	4.14	Yes
THIO-SS	20	15.11	15.25	14.44	14.06	15.75	18.50	14.69	13.56	15.17	76	1.51	4.53	No
pp'-DDT	25	23.50	22.12	22.25	21.88	22.75	21.50	22.00	21.38	22.17	89	0.69	2.07	No

February 10, 1994
Determination of MDL values for OC/CB "B" compounds. Normal spiking levels.

Compound	Spiked conc., (ng/L)	Recovery (ng/L)								ave. rec. %	std. dev (ng/L)	est. MDL (ng/L)	Accept. MDL ?
		1	2	3	4	5	6	7	8				
135-TCB	125	120.25	136.74	135.63	134.28	127.56	127.50	129.49	128.75	104	5.40	16.20	Yes
HCB	25	16.50	18.94	19.06	19.63	18.25	18.69	19.93	19.81	75	1.11	3.33	Yes
245-TCT	125	121.25	134.00	134.06	133.44	128.00	129.88	132.00	134.50	105	4.52	13.56	Yes
1245-TCB	25	25.44	26.19	27.25	27.50	28.88	28.69	26.44	28.31	109	1.25	3.75	Yes
CYCLOPENT	50	36.62	36.62	39.00	37.62	40.50	39.50	38.75	39.50	77	1.42	4.26	No
1234-TCB	25	26.31	29.94	28.81	28.44	26.81	27.88	28.31	28.50	112	1.14	3.42	Yes
HCB	25	21.69	26.00	24.62	24.06	24.81	23.56	25.50	25.19	98	1.35	4.05	Yes
LINDANE	25	17.88	22.75	21.08	21.08	20.38	19.88	20.94	20.29	82	1.37	4.11	Yes
ALDRIN	25	16.00	21.50	19.96	19.19	19.76	19.81	22.61	22.38	81	2.11	6.33	No
HEPTOXIDE	25	24.72	30.25	28.41	27.44	27.00	26.68	27.66	28.45	110	1.60	4.80	Yes
OCTA	25	16.19	21.12	20.44	19.38	21.75	20.35	23.19	23.38	83	2.30	6.90	No
THIODAN-1	50	47.08	56.13	53.22	51.5	52.02	51.61	54.16	55.72	105	2.88	8.64	Yes
pp'-DDE	125	88.20	113.06	111.18	105.56	121.04	112.10	120.42	123.24	89	11.27	33.81	No
ENDRIN	100	98.90	118.44	113.24	107.50	108.19	106.81	111.38	114.79	110	5.97	17.91	Yes
pp'-DDD	125	95.06	117.18	115.56	109.39	119.03	111.44	121.00	123.95	91	9.04	27.12	No
THIO-SS	100	89.88	106.30	104.62	103.25	94.98	96.75	100.12	102.82	100	5.57	16.71	Yes
pp'-DDT	125	80.75	102.56	99.46	89.38	105.54	99.18	108.06	112.08	80	10.22	30.66	No

March 12, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.2 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	5	3.29	3.44	3.70	3.60	3.74	3.80	3.62	3.49	3.59	72	0.17	0.51	Yes
124-TCB	25	22.52	22.95	23.20	22.95	23.65	23.54	23.32	23.12	23.16	93	0.36	1.08	No
123-TCB	25	23.65	23.28	24.59	23.36	23.93	24.18	23.61	23.66	23.78	95	0.435	1.31	No
236-TCT	25	21.86	22.56	23.68	22.85	23.50	25.70	23.96	23.45	23.45	94	1.14	3.41	Yes
1235-TCB	5	4.71	4.72	5.08	4.88	4.88	5.21	5.05	5.03	4.95	99	0.18	0.53	Yes
260-TCT	25	23.99	24.44	24.23	24.27	24.35	24.51	24.57	24.41	24.34	97	0.18	0.55	No
PENTA	5	5.28	4.75	4.66	4.71	4.86	4.83	4.74	5.29	4.89	98	0.25	0.76	Yes
α-BHC	5	4.62	4.73	4.69	4.66	4.69	4.72	4.88	4.74	4.72	94	0.08	0.24	No
HEPTACHLOR	5	3.92	4.00	4.04	4.07	4.26	4.29	4.18	4.18	4.12	82	0.13	0.39	No
OXYCHLOR	10	9.13	9.09	9.27	9.14	9.13	9.36	9.41	9.19	9.22	92	0.12	0.36	No
γ-CHLORDAN	10	9.30	9.21	9.21	9.08	9.13	9.34	9.48	9.20	9.24	92	0.13	0.39	No
α-CHLORDAN	10	9.42	9.40	9.41	9.38	9.25	9.52	9.56	9.33	9.41	94	0.10	0.30	No
DIELDRIN	10	10.40	10.61	10.04	10.01	9.85	10.19	10.64	10.28	10.25	103	0.29	0.87	No
op' -DDT	25	20.60	20.31	20.71	20.42	19.71	20.50	20.67	20.20	20.39	82	0.33	0.99	No
THIODAN-2	20	20.10	20.94	20.90	19.82	19.35	19.92	20.72	20.21	20.25	101	0.57	1.71	No
MIREX	25	22.21	21.57	21.58	21.63	20.56	21.97	22.02	20.83	21.55	86	0.58	1.74	No
METHOXY	25	21.43	22.40	22.66	22.05	20.85	21.80	22.24	21.94	21.92	88	0.57	1.71	No

March 12, 1994
Determination of MDL values for OC/CB "A" compounds. Spiked at 0.4 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ava. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	10	8.50	9.00	8.95	8.80	8.70	8.60	8.30	8.45	8.66	87	0.25	0.75	No
124-TCB	50	49.75	52.60	52.85	51.45	52.90	52.30	52.10	51.90	51.98	104	1.03	3.09	No
123-TCB	50	49.90	53.75	52.35	51.50	53.20	51.30	53.15	51.75	52.11	104	1.26	3.78	No
236-TCT	50	50.50	51.70	53.75	51.60	53.75	51.30	50.65	53.30	52.07	104	1.34	4.02	No
1235-TCB	10	11.20	10.90	11.00	11.50	10.90	10.85	10.80	10.85	11.00	110	0.24	0.72	No
260-TCT	50	51.40	52.15	52.85	52.65	52.95	52.25	52.70	52.60	52.44	105	0.50	1.50	No
PENTA	10	10.20	10.05	10.95	10.15	10.10	10.85	11.05	10.95	10.54	105	0.45	1.35	Yes
α -BHC	10	10.25	10.45	10.75	10.50	10.45	10.30	10.55	10.25	10.44	104	0.17	0.51	No
HEPTACHLOR	10	8.60	8.90	9.35	9.30	9.30	9.00	9.20	8.75	9.05	90	0.28	0.84	No
OXYCHLOR	20	18.85	19.45	19.85	20.00	19.60	19.30	20.25	19.20	19.56	98	0.46	1.38	No
γ -CHLORDAN	20	18.80	19.30	19.65	19.85	19.45	19.15	20.20	19.05	19.43	97	0.46	1.38	No
α -CHLORDAN	20	19.10	19.65	20.00	20.10	19.75	19.45	20.50	19.45	19.75	99	0.44	1.32	No
DIELDRIN	20	21.80	22.30	22.90	23.05	22.25	21.75	22.05	22.00	22.26	111	0.48	1.44	No
op'-DDT	50	41.65	43.15	43.70	44.70	42.45	42.20	45.15	42.35	43.17	86	1.25	3.75	No
THIODAN-2	40	44.15	44.70	46.35	46.05	43.25	43.55	44.25	42.50	44.35	111	1.33	3.99	Yes
MIREX	50	39.65	41.40	42.10	44.00	42.55	42.10	40.80	46.20	42.35	85	2.01	6.03	Yes
METHOXY	50	49.65	49.75	52.55	52.70	50.45	49.05	50.45	49.85	50.56	101	1.35	4.05	No

March 14, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.02 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev. (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	0.5	0.49	0.48	0.48	0.47	0.52	0.48	0.46	0.47	0.48	96	0.02	0.06	Yes
124-TCB	2.5	3.06	3.35	3.22	3.24	3.19	3.21	3.33	3.21	3.23	129	0.09	0.27	Yes
123-TCB	2.5	3.38	3.04	2.94	2.89	2.73	2.76	3.19	2.91	2.98	119	0.22	0.66	No
236-TCT	2.5	2.88	2.96	3.44	3.11	3.02	2.91	2.80	3.24	3.05	122	0.21	0.63	No
1235-TCB	0.5	0.58	0.73	0.72	0.69	0.62	0.76	0.60	0.79	0.69	137	0.08	0.24	No
26α-TCT	2.5	2.79	2.81	2.67	2.81	2.69	2.67	2.86	2.52	2.73	109	0.11	0.33	Yes
PENTA	0.5	0.70	0.49	0.66	0.68	0.63	0.48	0.66	0.73	0.63	125	0.09	0.27	No
α-BHC	0.5	0.51	0.51	0.50	0.50	0.50	0.49	0.51	0.51	0.50	100	0.007	0.02	No
HEPTACHLOR	0.5	0.48	0.45	0.45	0.55	0.48	0.48	0.49	0.48	0.48	96	0.03	0.09	Yes
OXYCHLOR	1	1.06	1.05	1.08	1.04	1.23	1.05	1.07	1.10	1.08	108	0.06	0.18	Yes
γ-CHLORDAN	1	1.06	1.11	1.12	1.13	1.10	1.15	1.15	1.16	1.12	112	0.03	0.09	No
α-CHLORDAN	1	1.13	1.13	1.09	1.06	1.13	1.11	1.08	1.08	1.10	110	0.03	0.09	No
DIELDRIN	1	1.15	1.35	1.12	1.14	1.10	1.30	1.11	1.18	1.18	118	0.09	0.27	No
op'-DDT	2.5	1.92	1.88	1.79	1.86	1.92	1.92	1.87	2.00	1.90	76	0.06	0.18	No
THIODAN-2	2	2.38	2.30	2.26	2.30	2.25	2.49	2.28	2.31	2.32	116	0.08	0.24	Yes
MIREX	2.5	2.56	2.57	2.73	2.51	2.39	2.46	2.54	2.64	2.55	102	0.11	0.33	Yes
METHOXY	2.5	2.20	2.10	1.99	1.98	1.84	1.98	1.97	2.01	2.01	80	0.11	0.33	Yes

March 15, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.04 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ava. rec. (ng/L)	ava. % rec.	std. dev. (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	1	0.91	0.88	0.84	0.84	0.85	0.84	0.90	0.85	0.86	86	0.03	0.09	No
124-TCB	5	5.88	6.02	5.87	5.87	5.73	5.37	5.94	5.77	5.81	116	0.20	0.60	Yes
123-TCB	5	5.40	4.68	5.78	5.43	5.96	5.39	5.54	5.59	5.47	109	0.38	1.14	No
236-TCB	5	5.72	5.78	4.90	4.75	4.99	5.06	5.35	6.01	5.32	106	0.47	1.41	No
1235-TCB	1	1.21	1.11	1.31	1.11	1.08	1.04	1.18	1.06	1.14	114	0.09	0.27	No
26 α -TCB	5	5.13	5.15	5.44	5.40	5.40	5.39	5.12	5.36	5.30	106	0.14	0.42	No
PENTA	1	1.05	1.15	1.22	1.05	1.25	1.04	1.13	1.25	1.14	114	0.09	0.27	No
α -BHC	1	0.99	0.97	0.99	0.97	0.98	0.94	1.00	0.99	0.98	98	0.02	0.06	No
HEPTACHLOR	1	0.87	0.89	0.90	0.84	0.97	1.03	1.03	0.90	0.93	93	0.07	0.21	No
OXYCHLOR	2	2.09	2.04	1.99	1.96	2.01	2.34	2.34	1.99	2.09	105	0.16	0.48	No
γ -CHLORDAN	2	1.96	2.03	2.05	2.07	2.13	2.22	2.24	2.10	2.10	105	0.10	0.30	Yes
α -CHLORDAN	2	2.11	2.10	2.07	2.07	2.05	2.21	2.31	2.17	2.14	107	0.09	0.27	Yes
DIELDRIN	2	2.44	2.45	2.20	2.42	2.59	2.35	2.53	2.45	2.43	121	0.12	0.36	Yes
op'-DDT	5	3.70	3.66	3.80	3.74	3.99	4.43	4.14	3.84	3.91	78	0.26	0.78	Yes
THIODAN-2	4	4.57	4.55	4.46	4.39	4.44	4.97	4.88	4.74	4.62	116	0.21	0.63	Yes
MIREX	5	5.11	5.11	5.17	5.39	5.41	5.18	5.63	5.54	5.32	106	0.20	0.60	Yes
METHOXY	5	4.97	3.94	4.19	3.97	4.30	4.80	4.42	4.28	4.36	87	0.37	1.11	No

March 15, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.06 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	1.5	1.73	1.88	1.74	1.71	1.66	1.75	1.67	1.78	1.74	116	0.07	0.21	Yes
124-TCB	7.5	8.58	8.57	8.50	8.57	8.73	8.45	8.62	8.59	8.58	114	0.08	0.24	No
123-TCB	7.5	8.14	8.46	8.24	8.03	7.95	8.72	8.33	8.06	8.24	110	0.26	0.78	Yes
236-TCT	7.5	8.82	7.45	8.41	7.91	8.69	8.79	7.71	7.12	8.11	108	0.66	1.98	No
1235-TCB	1.5	1.60	1.98	1.77	1.66	1.66	1.59	1.63	1.74	1.70	114	0.13	0.39	No
26 α -TCT	7.5	8.50	8.46	8.36	8.47	8.44	8.60	8.35	8.46	8.45	113	0.08	0.24	No
PENTA	1.5	1.72	1.36	1.69	1.49	1.68	1.69	1.60	1.55	1.60	107	0.12	0.36	No
α -BHC	1.5	1.59	1.56	1.56	1.60	1.59	1.59	1.57	1.67	1.59	106	0.04	0.12	No
HEPTACHLOR	1.5	1.55	1.53	1.59	1.46	1.45	1.48	1.39	1.52	1.50	100	0.06	0.18	Yes
OXYCHLOR	3	3.26	3.26	3.37	3.28	3.39	3.61	3.32	3.36	3.36	112	0.12	0.36	Yes
γ -CHLORDAN	3	3.28	3.34	3.45	3.37	3.45	3.43	3.39	3.44	3.39	113	0.06	0.18	No
α -CHLORDAN	3	3.36	3.33	3.40	3.32	3.48	3.41	3.41	3.46	3.40	113	0.06	0.18	No
DIELDRIN	3	3.47	3.40	3.68	3.74	3.84	3.50	3.86	3.66	3.64	121	0.17	0.51	Yes
op'-DDT	7.5	6.49	6.68	6.87	6.75	6.94	6.76	6.82	6.92	6.78	90	0.15	0.45	No
THIODAN-2	6	7.44	6.89	7.54	7.41	7.59	7.28	7.39	7.22	7.35	122	0.22	0.66	Yes
MIREX	7.5	8.61	8.84	9.10	9.17	9.26	9.21	8.97	8.97	9.02	120	0.22	0.66	No
METHOXY	7.5	6.36	6.23	6.66	6.60	6.85	6.73	6.28	6.45	6.52	87	0.22	0.66	No

March 22, 1994
Determination of MDL values for OC/CB "B" compounds. Normal spiking levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	125	119.38	119.20	114.43	116.02	117.54	114.82	112.79	113.30	115.94	93	2.55	7.65	No
HCB	25	18.75	18.62	17.63	17.64	18.45	18.18	18.28	17.62	18.15	73	0.46	1.38	No
245-TCT	125	120.54	118.95	115.56	117.29	119.24	118.71	115.94	115.78	117.75	94	1.87	5.61	No
1245-TCB	25	25.33	24.18	23.95	24.51	25.75	23.98	24.39	23.73	24.48	98	0.71	2.13	No
CYCLOPENT	50	36.30	35.01	35.92	33.95	39.48	37.43	35.96	33.81	35.98	72	1.86	5.58	Yes
1234-TCB	25	25.49	25.91	25.11	25.35	26.08	25.34	24.88	24.99	25.39	102	0.42	1.26	No
HC	25	22.38	22.28	21.91	22.43	21.93	21.96	24.24	22.54	22.46	90	0.76	2.28	No
LINDANE	25	25.26	25.65	25.52	25.58	25.58	25.43	24.69	25.14	25.36	101	0.32	0.96	No
ALDRIN	25	19.11	18.39	19.71	19.14	18.84	20.46	22.65	19.91	19.78	79	1.33	3.99	Yes
HEPTOXIDE	25	26.36	26.01	26.02	26.24	25.75	25.68	26.68	25.78	26.06	104	0.34	1.02	No
OCTA	25	20.04	18.40	20.41	19.13	19.08	20.94	22.52	20.58	20.14	81	1.30	3.90	Yes
THIODAN-1	50	52.01	51.27	51.16	51.85	51.05	51.58	53.18	51.60	51.71	103	0.68	2.04	No
pp'-DDE	125	101.95	96.81	106.02	99.70	99.57	108.52	122.40	107.78	105.34	84	8.07	24.21	Yes
ENDRIN	100	105.10	105.58	105.55	106.33	104.54	107.16	109.40	107.25	106.36	106	1.55	4.65	No
pp'-DDD	125	116.94	116.46	115.88	117.65	115.10	117.18	131.71	118.89	118.73	95	5.36	16.08	Yes
THIO-SS	100	111.45	111.88	108.78	111.44	109.79	111.34	109.16	110.08	110.49	110	1.18	3.54	No
pp'-DDT	125	103.09	97.82	107.50	102.84	101.57	110.11	125.42	110.56	107.36	86	8.51	25.53	No

March 23, 1994

Determination of MDL values for OC/CB "B" compounds. Spiked at 0.4 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept. MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	50	52.03	51.74	52.12	52.41	51.32	49.72	49.86	48.81	51.00	102	1.35	4.05	No
HCB	10	8.12	7.88	8.14	8.11	8.58	7.42	7.13	7.24	7.83	72	0.51	1.53	Yes
245-TCT	50	52.93	53.90	53.58	56.20	52.94	51.82	53.92	53.57	53.61	107	1.25	3.75	No
1245-TCB	10	10.58	10.89	10.46	11.34	10.57	11.31	11.11	10.98	10.90	109	0.34	1.02	Yes
CYCLOPENT	20	17.99	16.17	16.48	16.37	15.01	15.36	14.52	16.20	16.01	80	1.07	3.21	Yes
1234-TCB	10	11.07	11.01	11.07	11.17	10.94	10.92	10.91	10.99	11.01	110	0.09	0.27	No
HCB	10	9.82	9.54	9.80	9.63	9.73	9.93	9.66	9.94	9.76	98	0.14	0.42	No
LINDANE	10	10.92	10.70	10.91	10.68	10.81	10.69	10.67	10.73	10.76	108	0.10	0.30	No
ALDRIN	10	8.30	7.86	8.25	7.89	8.20	8.57	8.12	8.66	8.23	82	0.29	0.87	No
HEPTOXIDE	10	11.04	10.94	10.97	10.93	11.00	11.36	11.14	11.5	11.11	111	0.21	0.63	No
OCTA	10	8.38	7.79	8.36	7.90	8.09	8.30	7.70	8.54	8.13	81	0.31	0.93	No
THIODAN-1	20	22.34	22.12	22.09	22.01	22.22	22.44	22.83	22.92	22.37	112	0.34	1.02	No
pp'-DDE	50	44.22	42.04	44.17	42.72	44.02	46.43	44.26	47.19	44.38	89	1.71	5.13	Yes
ENDRIN	40	45.18	45.39	45.40	45.27	45.88	45.73	45.62	45.76	45.53	114	0.25	0.75	No
pp'-DDD	50	50.79	49.89	49.96	49.59	51.12	52.43	51.69	53.43	51.11	102	1.35	4.05	No
THIO-SS	40	47.88	47.42	47.45	46.83	47.92	47.65	48.33	48.37	47.73	119	0.51	1.53	No
pp'-DDT	50	42.05	39.84	42.06	40.36	42.01	44.72	43.13	45.84	42.50	85	2.03	6.09	Yes

March 25, 1994

Determination of MDL values for OC/CB "B" compounds. Normal spiking levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	125	116.77	116.95	116.05	119.41	117.64	117.34	115.18	113.19	116.57	93	1.84	5.52	No
HCB	25	17.36	17.29	17.29	17.62	17.71	17.41	16.53	16.28	17.19	69	0.51	1.53	No
245-TCT	125	117.54	119.38	118.65	120.85	118.37	119.13	117.07	115.39	118.30	95	1.65	4.95	No
1245-TCB	25	23.95	24.86	24.76	25.42	24.16	25.60	24.26	24.04	24.63	99	0.63	1.89	No
CYCLOPENT	50	14.20	12.95	14.99	16.05	13.69	14.71	13.34	12.77	14.09	28	1.12	3.36	No
1234-TCB	25	24.84	25.47	24.98	25.80	24.78	25.17	24.72	24.83	25.07	100	0.38	1.14	No
HCB	25	21.60	20.99	21.82	21.41	21.30	21.57	21.91	21.75	21.54	86	0.30	0.90	No
LINDANE	25	24.53	24.60	24.44	24.75	24.81	24.00	24.79	24.61	24.57	98	0.26	0.78	No
ALDRIN	25	16.43	15.51	16.86	16.29	16.72	16.32	17.32	16.78	16.53	66	0.53	1.59	No
HEPTOXIDE	25	25.93	25.58	26.11	26.35	26.00	25.89	25.86	25.88	25.95	104	0.22	0.66	No
OCTA	25	15.34	14.08	16.18	15.51	15.26	14.90	15.85	16.06	15.40	62	0.68	2.04	No
THIODAN-1	50	50.70	50.54	51.62	52.49	51.41	51.06	51.46	51.71	51.37	103	0.62	1.86	No
pp'-DDE	125	85.91	79.15	88.42	86.68	85.08	82.54	89.45	89.04	85.80	69	3.50	10.50	No
ENDRIN	100	105.97	99.83	106.16	105.96	106.03	101.51	102.21	104.19	103.60	104	2.30	6.90	No
pp'-DDD	125	110.29	106.16	111.60	111.65	110.99	111.29	112.18	112.41	110.80	89	2.00	6.00	No
THIO-SS	100	100.15	99.39	99.97	103.61	101.92	99.50	100.31	101.87	100.80	101	1.48	4.44	No
pp'-DDT	125	88.16	81.40	91.09	91.40	87.56	84.73	94.46	92.74	88.90	71	4.35	13.05	Yes

May 7, 1994

Determination of MDL values for OC/CB "B" compounds. Spiked at 0.12 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	15	19.82	21.03	19.72	19.18	18.19	21.30	17.99	19.66	19.61	131	1.18	3.54	No
HCBD	3	3.85	3.25	3.53	3.51	3.53	3.48	3.42	3.23	3.48	116	0.19	0.57	Yes
245-TCT	15	20.37	18.53	18.97	18.42	18.78	18.90	18.47	18.93	18.92	126	0.62	1.86	Yes
1245-TCB	3									nd*				
CYCLOPENT	6									nd*				
1234-TCB	3	4.02	4.64	4.36	3.93	4.16	4.22	4.32	3.90	4.19	140	0.25	0.75	No
HCB	3	4.12	3.98	4.05	3.76	4.08	4.27	4.23	4.02	4.06	135	0.16	0.48	Yes
LINDANE	3	3.31	3.28	3.40	3.21	3.34	3.39	3.24	3.48	3.33	111	0.09	0.27	No
ALDRIN	3	3.55	3.46	3.60	3.41	3.58	3.59	3.46	3.51	3.52	117	0.07	0.21	No
HEPTOXIDE	3	3.90	3.87	3.96	3.81	3.96	3.87	3.86	3.89	3.89	130	0.05	0.15	No
OCTA	3	3.67	3.44	3.63	3.40	3.63	3.57	3.51	3.52	3.55	118	0.10	0.30	Yes
THIODAN-1	6	7.56	7.35	7.56	7.62	7.79	7.51	7.38	7.58	7.54	126	0.14	0.42	No
pp'-DDE	15	18.32	18.17	18.66	17.75	18.63	18.36	17.93	18.67	18.31	122	0.35	1.05	No
ENDRIN	12	15.54	15.31	15.73	15.61	15.86	15.54	15.36	15.65	15.58	130	0.18	0.54	No
pp'-DDD	15	18.63	18.60	19.40	18.45	19.36	18.74	18.51	19.32	18.88	126	0.41	1.23	No
THIO-SS	12	12.34	12.29	12.82	12.08	12.81	12.30	12.07	12.94	12.46	104	0.35	1.05	No
pp'-DDT	15	14.95	15.11	15.14	14.46	15.20	14.81	14.42	15.16	14.91	99	0.31	0.93	No

*not detected

May 7, 1994

Determination of MDL values for OC/CB "B" compounds. Spiked at 0.8 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	100	93.63	96.72	98.84	91.45	90.30	95.35	93.64	90.27	93.78	94	3.08	9.24	No
HCBD	20	16.29	17.90	17.47	15.48	14.55	17.77	15.61	15.45	16.32	82	1.25	3.75	Yes
245-TCT	100	102.09	104.82	102.45	99.49	100.26	103.43	100.49	97.60	101.33	101	2.32	6.96	No
1245-TCB	20	20.70	20.94	20.46	20.38	20.17	20.33	20.57	20.07	20.45	102	0.28	0.84	No
CYCLOPENT	40	29.70	33.46	38.77	30.18	30.32	33.44	31.10	30.40	32.17	80	3.04	9.12	No
1234-TCB	20	21.44	21.55	20.48	20.52	21.43	21.04	21.42	21.04	21.12	106	0.42	1.26	No
HCB	20	18.70	19.80	17.47	18.76	19.24	19.35	18.79	18.44	19.07	95	0.46	1.38	No
LINDANE	20	20.56	20.18	20.36	19.81	19.98	20.22	20.60	19.68	20.17	101	0.33	0.99	No
ALDRIN	20	15.59	17.88	17.60	15.84	16.13	17.38	15.43	15.45	16.41	82	1.03	3.09	Yes
HEPTOXIDE	20	21.07	21.46	21.42	20.42	21.47	21.46	21.60	20.84	21.22	106	0.41	1.23	No
OCTA	20	14.93	16.96	17.18	15.00	15.85	16.86	15.13	14.98	15.86	79	0.99	2.97	Yes
THIODAN-1	40	39.86	41.34	41.21	39.03	41.58	40.83	41.17	40.20	40.65	102	0.88	2.64	No
pp'-DDE	100	78.01	89.62	89.16	78.77	85.71	88.32	80.26	79.89	83.72	84	4.98	14.93	Yes
ENDRIN	80	84.48	86.30	87.20	79.64	85.99	86.13	86.98	82.94	84.96	106	2.56	7.69	No
pp'-DDD	100	93.50	100.94	100.31	91.20	99.79	101.23	97.69	94.53	97.40	97	3.84	11.53	Yes
THIO-SS	80	85.41	86.63	88.20	79.36	89.47	89.61	91.24	82.89	86.60	108	3.95	11.84	Yes
pp'-DDT	100	78.07	89.83	89.98	77.28	86.19	89.13	80.38	79.10	83.74	84	5.58	16.73	Yes

May 8, 1994

Determination of MDL values for OC/CB "B" compounds. Spiked at 0.08 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev. (ng/L)	est. MDL (ng/L)	Accept. MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	10	13.80	13.13	12.66	14.08	12.62	12.58	12.26	12.25	12.92	129	0.69	2.07	No
HCB	2	2.45	2.59	2.42	2.44	2.09	2.11	2.16	2.43	2.34	117	0.19	0.57	No
245-TCT	10	13.65	12.30	12.31	12.91	11.45	11.73	11.49	12.15	12.25	122	0.75	2.25	No
1245-TCB	2									nd*				
CYCLOPENT	4									nd*				
1234-TCB	2	2.70	2.53	2.61	3.07	2.55	2.56	2.79	2.25	2.63	132	0.24	0.72	No
HCB	2	2.86	2.91	3.10	2.83	2.77	2.64	2.86	2.74	2.84	142	0.14	0.42	No
LINDANE	2	2.18	2.13	2.30	2.19	2.18	2.18	2.21	2.03	2.18	109	0.08	0.24	Yes
ALDRIN	2	2.30	2.14	2.29	2.24	2.17	2.28	2.23	2.28	2.24	112	0.06	0.18	No
HEPTOXIDE	2	2.44	2.54	2.33	2.45	2.52	2.67	2.60	2.57	2.52	126	0.11	0.33	Yes
OCTA	2	2.41	2.20	2.34	2.26	2.27	2.35	2.34	2.37	2.32	116	0.07	0.21	Yes
THIODAN-1	4	5.04	4.79	4.87	4.60	4.09	5.09	4.22	4.86	4.70	118	0.37	1.11	No
pp'-DDE	10	12.11	11.02	11.47	11.24	11.64	12.23	11.86	11.82	11.67	117	0.42	1.26	Yes
ENDRIN	8	10.15	9.88	9.68	9.37	9.99	10.07	10.27	9.59	9.88	124	0.31	0.93	Yes
pp'-DDD	10	12.23	11.72	11.48	11.35	11.90	12.38	12.09	11.88	11.88	119	0.36	1.08	Yes
THIO-SS	8	8.21	8.43	7.55	7.65	8.13	8.22	8.38	7.71	8.04	101	0.35	1.05	Yes
pp'-DDT	10	9.24	8.53	8.93	8.74	9.46	9.65	9.38	9.37	9.16	92	0.39	1.17	Yes

*not detected

May 9, 1994

Determination of MDL values for OC/CB "B" compounds. Spiked at 0.04 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	5	6.65	6.68	6.34	5.41	7.16	5.89	6.48	6.32	6.37	127	0.53	1.59	No
HCBD	1	1.16	1.22	1.02	0.97	1.07	1.11	1.15	1.03	1.09	109	0.08	0.24	No
245-TCT	5	6.04	6.50	6.16	5.78	6.36	6.84	6.46	5.85	6.25	125	0.36	1.08	No
1245-TCB	1									nd*				
CYCLOPENT	2									nd*				
1234-TCB	1									nd*				
HCB	1	1.45	1.60	1.64	1.49	1.75	1.47	1.39	1.29	1.51	151	0.15	0.45	No
LINDANE	1	1.19	1.14	1.10	1.19	1.06	1.13	1.11	1.11	1.13	113	0.045	0.14	Yes
ALDRIN	1	1.23	1.22	1.21	1.18	1.18	1.16	1.23	1.19	1.20	120	0.03	0.09	No
HEPTOXIDE	1	1.31	1.30	1.32	1.34	1.25	1.24	1.25	1.31	1.29	129	0.04	0.12	Yes
OCTA	1	1.23	1.25	1.23	1.23	1.19	1.14	1.16	1.24	1.21	121	0.04	0.12	Yes
THIODAN-1	2	2.61	2.52	2.61	2.41	2.69	2.59	2.44	2.75	2.58	129	0.12	0.36	Yes
pp'-DDE	5	6.91	6.44	6.58	6.44	6.24	6.08	6.12	6.27	6.38	128	0.27	0.81	Yes
ENDRIN	4	5.78	5.78	5.76	5.89	5.41	5.30	5.32	5.54	5.60	140	0.23	0.69	Yes
pp'-DDD	5	7.74	6.76	7.13	6.92	6.55	6.30	6.22	6.37	6.75	135	0.51	1.53	No
THIO-SS	4	5.33	4.66	4.75	4.78	4.46	4.29	4.28	4.19	4.59	115	0.37	1.11	No
pp'-DDT	5	5.40	4.83	5.17	4.84	4.50	4.52	4.41	4.44	4.76	95	0.37	1.11	No

*not detected

June 2, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.1 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	2.5	2.72	2.5	2.44	2.53	2.52	2.72	2.47	2.47	2.55	102	0.111	0.33	Yes
124-TCB	12.5	14.52	14.41	14.90	14.40	14.395	15.17	14.13	14.25	14.52	116	0.345	1.03	No
123-TCB	12.5	13.11	13.46	13.60	13.20	13.17	13.70	12.86	12.995	13.26	106	0.30	0.90	No
236-TCT	12.5	13.83	16.55	13.95	14.94	14.43	12.06	14.69	14.17	14.33	115	1.25	3.76	No
1235-TCB	2.5	2.36	3.75	3.32	3.18	3.06	3.08	3.11	2.93	3.10	124	0.388	1.16	No
26 α -TCT	12.5	13.26	13.80	13.29	13.24	13.64	15.01	13.24	13.26	13.59	109	0.61	1.83	Yes
PENTA	2.5	3.04	3.03	3.02	3.25	3.11	2.74	2.86	3.05	3.01	120	0.15	0.46	Yes
α -BHC	2.5	2.38	2.39	2.42	2.37	2.37	2.57	2.51	2.52	2.44	98	0.08	0.24	No
HEPTACHLOR	2.5	2.50	2.47	2.49	2.55	2.55	3.07	2.62	2.57	2.60	104	0.19	0.58	No
OXYCHLOR	5	5.29	5.36	5.18	5.45	5.37	5.39	5.44	5.56	5.38	108	0.113	0.34	No
γ -CHLORDAN	5	5.17	5.19	5.00	5.28	5.19	5.21	5.26	5.33	5.20	104	0.10	0.30	No
α -CHLORDAN	5	5.20	5.21	5.29	5.38	5.21	5.22	5.29	5.49	5.29	106	0.103	0.31	No
DIELDRIN	5	5.60	5.51	5.52	5.63	5.63	5.46	5.55	5.65	5.57	111	0.069	0.21	No
op'-DDT	12.5	11.33	11.23	10.76	11.54	11.28	11.19	11.57	11.52	11.30	90	0.264	0.79	No
THIODAN-2	10	9.20	8.84	8.96	9.03	9.28	8.77	8.89	8.94	8.99	90	0.175	0.52	No
MIREX	12.5	12.07	12.58	12.37	12.79	12.54	12.30	12.25	12.14	12.38	99	0.242	0.72	No
METHOXY	12.5	11.55	11.13	10.77	11.40	11.44	11.28	11.57	11.45	11.32	91	0.265	0.80	No

June 2, 1994
Determination of MDL values for OC/CB "A" compounds. Spiked at 0.8 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	20	19.24	18.02	17.78	18.49	18.99	18.65	18.60	18.16	18.49	92	0.49	1.47	No
124-TCB	100	99.78	97.46	95.59	97.76	100.64	97.68	98.51	96.50	97.99	98	1.64	4.93	No
123-TCB	100	97.45	94.95	96.65	95.31	99.64	94.62	96.83	96.35	96.48	96	1.61	4.85	No
236-TCT	100	95.94	96.27	94.11	95.24	96.45	96.38	96.05	95.33	95.72	96	0.79	2.38	No
1235-TCB	20	19.76	20.03	19.88	20.47	20.13	20.10	20.62	20.11	20.14	101	0.28	0.85	No
26 α -TCT	100	97.53	96.73	95.15	97.82	99.52	96.96	97.58	97.83	97.39	97	1.23	3.69	No
PENTA	20	17.11	17.23	17.13	16.86	16.59	17.20	17.40	16.88	17.05	85	0.26	0.77	No
α -BHC	20	18.77	19.34	18.66	19.15	18.59	19.46	19.15	18.64	18.97	95	0.34	1.03	No
HEPTACHLOR	20	13.72	14.34	15.38	14.28	13.19	15.59	15.20	14.60	14.54	73	0.83	2.50	Yes
OXYCHLOR	40	27.74	28.97	30.76	28.15	25.27	31.41	30.28	29.21	28.97	72	1.96	5.87	Yes
γ -CHLORDAN	40	25.51	27.06	29.13	26.18	22.97	29.74	28.14	27.11	36.98	67	2.15	6.46	Yes
α -CHLORDAN	40	27.19	28.53	30.17	27.52	24.19	30.77	29.53	28.24	28.27	71	2.07	6.20	Yes
DIELDRIN	40	35.94	37.45	36.88	36.01	30.66	37.69	37.78	34.69	35.89	90	2.36	7.08	Yes
op'-DDT	100	57.35	62.75	67.90	60.58	57.12	70.24	66.18	61.70	62.98	63	4.79	14.4	Yes
THIODAN-2	80	69.55	73.00	69.58	70.51	48.07	72.04	73.11	66.15	67.75	85	8.27	24.8	No
MIREX	100	73.33	79.13	78.68	68.14	53.74	73.97	66.18	70.65	70.48	70	8.16	24.5	No
METHOXY	100	91.68	97.80	94.00	92.48	69.73	99.24	74.57	89.34	88.61	89	10.72	32.2	No

June 3, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.4 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev. (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	10	10.33	10.07	9.59	10.42	11.03	11.26	11.28	10.85	10.50	106	0.604	1.81	Yes
124-TCB	50	52.51	51.85	51.14	51.26	52.03	51.22	50.55	50.84	51.42	103	0.653	1.96	No
123-TCB	50	52.13	55.92	51.05	50.95	51.52	51.26	50.57	49.95	51.67	103	1.83	5.50	Yes
236-TCF	50	52.28	51.06	51.80	52.22	51.52	53.04	51.79	50.04	51.72	103	0.896	2.69	No
1235-TCB	10	10.68	10.86	10.65	11.14	10.61	11.30	10.82	10.39	10.81	108	0.295	0.89	No
26 α -TCF	50	50.91	51.44	49.87	50.53	50.39	50.66	49.48	49.40	50.36	101	0.677	2.03	No
PENTA	10	9.28	9.50	9.89	9.29	9.57	9.62	9.73	9.57	9.56	96	0.206	0.617	No
α -BHC	10	9.97	9.93	9.82	9.76	9.99	9.72	9.53	9.54	9.78	98	0.181	0.542	No
HEPTACHLOR	10	7.98	7.91	8.07	8.07	8.63	8.75	8.74	8.51	8.33	83	0.359	1.08	Yes
OXYCHLOR	20	16.10	15.99	16.13	16.26	17.40	17.40	17.68	17.43	16.80	84	0.735	2.20	Yes
γ -CHLORDAN	20	15.33	15.20	15.41	15.45	16.70	16.75	16.95	16.79	16.07	80	0.782	2.34	Yes
α -CHLORDAN	20	16.01	15.61	15.91	16.03	17.22	17.25	17.44	17.28	16.59	83	0.766	2.30	Yes
DIELDRIN	20	19.80	19.60	19.10	19.42	20.29	20.23	20.14	20.06	19.83	99	0.427	1.28	No
op'-DDT	50	34.83	34.38	34.66	35.06	38.32	38.83	39.08	38.69	36.73	73	2.16	6.46	Yes
THIODAN-2	40	40.03	39.59	35.60	36.74	38.04	39.51	37.79	37.38	38.08	95	1.54	4.63	Yes
MIREX	50	39.82	37.51	35.44	37.04	38.11	36.66	37.89	35.95	37.30	75	1.37	4.11	No
METHOXY	50	48.32	47.90	44.93	46.21	50.14	49.41	50.28	49.52	48.34	97	1.92	5.77	Yes

June 3, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.2 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	est. MDL (ng/L)	Accept MDL?
		1	2	3	4	5	6	7	8				
HCE	5	4.92	4.88	4.91	4.81	4.95	4.91	4.86	4.73	4.87	.071	0.21	No
124-TCB	25	26.96	27.65	26.70	26.09	26.96	27.39	26.62	27.11	26.94	108	0.481	No
123-TCB	25	26.12	25.56	28.93	25.76	27.09	26.17	26.82	28.32	26.85	107	1.22	Yes
236-TCF	25	27.37	27.93	26.51	26.74	26.60	27.01	28.15	27.46	27.22	109	0.61	No
1235-TCB	5	5.41	5.66	5.58	5.59	5.57	5.82	6.21	6.34	5.77	115	0.33	Yes
26 α -TCF	25	26.32	27.22	26.23	26.07	26.50	26.60	27.24	26.98	26.64	107	0.45	No
PENTA	5	5.49	5.80	5.47	5.13	5.28	5.16	5.33	5.19	5.36	107	0.22	Yes
α -BHC	5	4.76	4.89	4.72	4.69	4.71	4.78	4.79	4.75	4.76	95	0.06	No
HEPTACHLOR	5	4.47	4.40	4.68	4.40	4.45	4.27	4.29	4.32	4.41	88	0.13	No
OXYCHLOR	10	9.29	9.11	9.10	9.08	9.22	8.91	8.89	8.98	9.07	91	0.14	No
γ -CHLORDAN	10	8.94	8.69	8.65	8.55	8.73	8.45	8.33	8.50	8.61	86	0.19	No
α -CHLORDAN	10	9.09	9.02	9.03	8.96	8.90	8.61	8.66	8.93	8.90	89	0.17	No
DIELDRIN	10	10.68	10.82	10.63	10.63	10.54	10.58	10.73	10.22	10.60	106	0.18	No
op'-DDT	25	20.03	19.51	19.68	19.25	19.51	19.26	18.29	18.76	19.29	77	0.545	No
THIODAN-2	20	20.07	20.83	20.92	20.51	20.13	21.02	20.35	20.02	20.56	103	0.37	No
MIREX	25	20.64	20.29	20.43	19.80	19.82	21.90	19.90	19.84	20.33	81	0.71	No
METHOXY	25	25.08	24.63	25.16	24.98	24.90	27.01	24.72	23.66	25.02	100	0.93	Yes

June 6, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.08 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. & rec.	std. dev. (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	2	1.98	2.18	1.93	1.97	2.22	1.91	2.02	2.49	2.11	106	0.20	0.60	No
124-TCB	10	11.04	11.20	11.03	11.27	11.79	10.96	10.83	11.77	11.24	112	0.36	1.09	Yes
123-TCB	10	10.22	10.38	10.38	10.87	10.24	10.98	9.99	10.27	10.42	104	0.34	1.01	Yes
236-TCT	10	11.53	11.03	10.57	11.67	11.16	10.85	11.52	9.35	10.96	110	0.75	2.25	No
1235-TCB	2	2.28	2.63	2.58	2.38	2.66	2.33	2.40	2.72	2.50	125	0.17	0.51	No
26 α -TCT	10	10.44	10.42	10.44	10.26	10.40	10.90	10.28	10.94	10.51	105	0.26	0.79	No
PENTA	2	2.24	2.35	2.38	2.36	2.44	2.28	2.27	2.92	2.40	120	0.22	0.65	No
α -BHC	2	1.93	1.87	1.87	2.01	1.98	1.83	1.86	1.91	1.91	95	0.06	0.18	No
HEPTACHLOR	2	1.99	2.02	1.92	2.09	1.96	1.88	1.98	2.03	1.98	99	0.065	0.20	Yes
OXYCHLOR	4	4.32	4.27	4.13	4.38	4.36	3.84	4.33	4.22	4.23	106	0.18	0.53	Yes
γ -CHLORDAN	4	4.14	4.00	3.87	4.17	4.18	3.60	4.04	4.05	4.01	100	0.19	0.58	Yes
α -CHLORDAN	4	4.20	4.08	3.93	4.21	4.23	3.62	4.13	4.18	4.07	102	0.21	0.62	Yes
DIELDRIN	4	4.47	4.13	4.20	4.49	4.44	3.69	4.45	4.25	4.26	107	0.27	0.81	Yes
op'-DDT	10	8.90	8.66	8.15	9.00	9.01	7.38	8.76	8.55	8.55	86	0.55	1.65	Yes
THIODAN-2	8	7.82	8.17	7.13	8.23	7.91	6.29	7.99	7.26	7.60	95	0.66	1.99	No
MIREX	10	10.62	9.88	10.01	10.35	10.90	8.04	10.62	10.31	10.09	101	0.89	2.68	No
METHOXY	10	9.48	8.67	7.95	8.87	9.33	6.81	9.62	8.45	8.65	86	0.93	2.79	No

June 6, 1994

Determination of MDL values for OC/CB "A" compounds. Spiked at 0.04 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	1	1.18	1.15	1.17	1.17	1.14	1.08	1.14	1.01	1.13	113	0.06	0.18	Yes
124-TCB	5	6.60	6.75	6.42	6.58	6.35	6.40	6.36	5.85	6.41	128	0.27	0.81	Yes
123-TCB	5	5.44	5.84	5.71	5.86	5.67	5.39	5.50	6.00	5.68	114	0.22	0.66	Yes
236-TCT	5	5.90	6.54	6.69	7.46	7.21	6.81	7.51	5.45	6.70	134	0.73	2.19	No
1235-TCB	1									nd*				
26 α -TCF	5	5.68	5.57	5.71	5.59	5.56	5.81	5.93	6.61	5.81	116	0.35	1.04	No
PENTA	1	1.65	1.62	1.60	1.62	1.54	1.63	1.87	1.50	1.63	163	0.11	0.33	No
α -BHC	1	1.02	1.03	1.02	1.01	1.01	1.06	0.89	1.37	1.05	105	0.14	0.41	No
HEPTACHLOR	1	1.02	1.03	1.03	1.00	1.07	1.04	1.02	0.99	1.02	102	0.024	0.07	No
OXYCHLOR	2	2.29	2.23	2.21	2.22	2.26	2.18	2.25	2.29	2.24	112	0.039	0.12	No
γ -CHLORDAN	2	2.12	2.08	2.06	2.05	2.10	2.08	2.13	2.43	2.13	106	0.12	0.37	Yes
α -CHLORDAN	2	2.19	2.20	2.13	2.11	2.38	2.12	2.18	2.17	2.18	109	0.086	0.26	Yes
DIELDRIN	2	2.33	2.33	2.30	2.27	2.33	2.27	2.31	2.29	2.30	115	0.026	0.08	No
op'-DDT	5	4.68	4.28	4.31	4.22	4.44	4.36	4.34	4.88	4.44	89	0.23	0.68	Yes
THIODAN-2	4	4.58	4.79	4.59	4.68	4.62	4.48	4.65	4.85	4.66	116	0.12	0.36	No
MIREX	5	6.00	6.16	6.08	5.66	5.81	5.71	5.85	5.44	5.84	117	0.24	0.71	Yes
METHOXY	5	4.57	4.37	4.39	4.32	4.32	4.08	4.67	4.34	4.38	88	0.18	0.53	Yes

* not detected.

June 8, 1994

Determination of MDL values for OC/CB "B" compounds. Spiked at 0.2 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	25	27.95	27.38	26.65	27.27	28.34	26.09	26.76	27.79	27.28	109	0.75	2.25	No
HCB	5	5.34	5.28	5.08	5.14	5.09	5.13	5.28	5.13	5.18	104	0.10	0.30	No
245-TCT	25	28.33	27.77	26.84	29.12	25.85	25.90	28.15	27.99	27.49	110	1.18	3.54	Yes
1245-TCB	5	6.43	6.33	6.15	6.18	6.49	5.29	4.94	5.76	5.95	119	0.57	1.71	No
CYCLOPENT	10									nd*				
1234-TCB	5	5.36	5.36	5.19	5.05	5.75	5.22	5.38	5.32	5.33	107	0.20	0.60	Yes
HCB	5	5.90	6.01	5.79	6.04	6.53	5.96	6.11	6.04	6.05	121	0.22	0.66	Yes
LINDANE	5	4.97	4.73	4.61	4.61	4.64	4.98	4.97	4.68	4.77	95	0.17	0.51	Yes
ALDRIN	5	5.39	5.36	5.30	5.34	5.20	5.28	5.34	5.28	5.31	106	0.06	0.18	No
HEPTOXIDE	5	5.75	5.76	5.68	5.71	5.72	5.73	5.76	5.76	5.73	115	0.03	0.09	No
OCTA	5	5.55	5.38	5.46	5.41	5.31	5.43	5.43	5.52	5.44	109	0.08	0.24	No
THIODAN-1	10	11.44	11.61	11.43	11.54	12.21	11.32	11.89	11.45	11.61	116	0.30	0.90	No
pp'-DDE	25	27.91	27.55	27.49	27.53	27.04	27.58	27.85	27.77	27.59	110	0.27	0.81	No
ENDRIN	20	24.65	24.81	24.93	24.61	23.75	24.38	25.25	24.41	24.60	123	0.44	1.32	No
pp'-DDD	25	28.69	28.60	28.48	28.53	28.29	28.61	28.78	28.62	28.58	114	0.15	0.45	No
THIO-SS	20	18.92	19.04	18.70	18.86	18.58	18.68	18.67	18.51	18.75	94	0.18	0.54	No
pp'-DDT	25	24.16	24.72	25.02	23.88	24.18	24.20	25.64	24.66	24.56	98	0.57	1.71	No

*not detected

June 9, 1994

Determination of MDL values for OC/CB "B" compounds. Spiked at 0.8 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ava. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	100	101.02	101.44	100.24	100.92	96.95	100.45	105.29	101.92	101.03	101	2.29	6.87	No
HCBD	20	18.73	19.10	18.52	18.54	18.75	18.68	18.93	19.06	18.79	94	0.22	0.66	No
245-TCF	100	103.81	104.83	105.25	104.04	98.94	100.68	103.74	103.74	103.13	103	2.17	6.51	No
1245-TCB	20	20.50	21.02	22.74	21.43	22.89	20.81	21.00	20.70	21.39	107	0.92	2.76	Yes
CYCLOPENT	40	33.78	31.98	32.36	35.40	35.75	30.49	33.00	38.23	33.87	85	2.48	7.44	Yes
1234-TCB	20	21.89	21.67	22.30	21.50	22.39	20.35	21.58	22.03	21.71	109	0.64	1.92	No
HCB	20	20.84	19.98	19.37	19.33	20.82	20.50	20.58	19.98	20.18	101	0.61	1.83	No
LINDANE	20	20.68	20.54	20.81	20.59	19.56	20.36	20.55	20.79	20.48	102	0.40	1.20	No
ALDRIN	20	19.35	18.74	18.17	18.15	18.58	18.84	20.26	19.09	18.90	94	0.69	2.07	Yes
HEPTOXIDE	20	21.70	21.46	21.26	21.23	21.11	21.47	22.38	21.80	21.55	108	0.41	1.23	No
OCTA	20	19.23	18.51	18.28	18.17	19.07	19.09	19.89	19.09	18.92	95	0.57	1.71	No
THIODAN-1	40	41.75	41.42	40.77	40.64	41.69	42.40	43.01	42.07	41.72	104	0.79	2.37	No
pp'-DDE	100	97.19	93.33	91.66	92.23	95.60	97.45	102.77	95.24	95.68	96	3.58	10.74	Yes
ENDRIN	80	88.85	86.12	86.68	86.74	86.39	87.45	91.15	89.55	87.87	110	1.80	5.40	No
pp'-DDD	100	104.12	101.52	97.53	98.84	100.69	104.93	108.95	103.45	102.50	102	3.65	10.95	Yes
THIO-SS	80	86.78	85.08	85.34	85.99	85.56	87.43	89.85	88.68	86.84	108	1.71	5.13	No
pp'-DDT	100	97.54	89.44	87.67	91.15	95.60	97.70	102.81	97.48	94.92	95	5.08	15.24	Yes

June 10, 1994
Determination of MDL values for OC/CB "B" compounds. Spiked at 0.4 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	50	52.02	56.76	54.37	54.72	54.55	55.36	52.67	52.17	54.08	108	1.67	5.01	Yes
HCB	10	9.95	10.20	10.24	10.03	10.21	10.31	10.07	9.85	10.11	101	0.16	0.48	No
245-TCT	50	54.68	55.77	55.23	55.17	54.75	57.72	54.55	54.21	55.26	111	1.10	3.30	No
1245-TCB	10	10.29	12.07	12.41	11.06	11.14	11.37	10.99	10.92	11.28	113	0.67	2.01	Yes
CYCLOPENT	20	18.17	17.91	21.86	18.47	18.41	18.13	19.68	21.42	19.26	96	1.57	4.71	No
1234-TCB	10	11.33	11.57	11.46	11.42	10.77	11.58	11.56	11.86	11.44	114	0.31	0.93	No
HCB	10	10.10	9.96	10.77	10.63	11.40	10.66	10.53	10.42	10.56	106	0.44	1.32	Yes
LINDANE	10	10.13	10.74	10.42	10.35	10.34	10.52	10.30	10.35	10.39	104	0.18	0.54	No
ALDRIN	10	8.55	8.79	9.81	9.37	9.75	9.75	9.57	8.92	9.31	93	0.49	1.47	Yes
HEPTOXIDE	10	9.53	10.74	10.77	10.82	10.65	10.90	10.79	10.71	10.61	106	0.44	1.32	Yes
OCTA	10	8.23	8.84	9.83	9.38	9.55	9.75	9.58	8.90	9.26	93	0.55	1.65	Yes
THIODAN-1	20	18.29	20.88	21.63	21.30	21.57	21.37	21.08	20.87	20.87	104	1.08	3.24	Yes
pp'-DDE	50	39.25	42.84	48.84	46.07	47.76	48.45	47.67	44.41	45.66	91	3.32	9.96	Yes
ENDRIN	40	35.21	44.62	45.33	43.94	42.71	45.97	43.82	42.15	42.97	107	3.38	10.14	No
pp'-DDD	50	41.61	49.03	52.25	50.78	51.37	52.40	51.42	49.49	49.79	100	3.52	10.56	No
THIO-SS	40	33.35	43.64	42.09	42.13	40.26	42.65	42.09	41.86	41.01	103	3.23	9.69	No
pp'-DDT	50	34.42	40.22	45.36	42.46	44.10	45.61	44.75	41.38	42.29	85	3.72	11.16	No

June 10, 1994
 Determination of MDL values for OC/CB "B" compounds. Spiked at 0.1 x normal levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev. (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	12.5	15.15	17.47	15.05	13.88	16.08	15.99	14.89	15.03	15.44	123	1.07	3.21	No
HCB	2.5	2.83	2.86	2.81	2.79	2.82	2.76	2.82	2.84	2.82	113	0.03	0.09	No
245-TCT	12.5	14.45	15.52	13.60	14.90	14.65	16.95	16.10	13.83	15.00	120	1.14	3.42	No
1245-TCB	2.5									nd*				
CYCLOPENT	5									nd*				
1234-TCB	2.5	2.79	2.86	2.98	2.75	2.84	2.98	2.97	2.53	2.84	114	0.15	0.45	Yes
HCB	2.5	3.29	3.28	3.23	3.42	3.26	3.59	3.20	3.21	3.31	132	0.13	0.39	Yes
LINDANE	2.5	2.90	2.72	2.64	2.65	2.75	2.81	2.85	2.69	2.75	110	0.10	0.30	Yes
ALDRIN	2.5	2.64	2.71	2.62	2.38	2.61	2.70	2.69	2.59	2.62	105	0.11	0.33	Yes
HEPTOXIDE	2.5	2.93	2.93	2.89	2.56	2.95	2.97	2.94	2.93	2.89	116	0.13	0.39	Yes
OCTA	2.5	2.72	2.84	2.67	2.45	2.72	2.89	2.79	2.64	2.72	109	0.14	0.42	Yes
THIODAN-1	5	5.99	6.06	6.01	5.20	5.99	6.42	6.11	6.06	5.98	120	0.34	1.02	No
pp'-DDE	12.5	13.24	13.40	13.23	10.88	13.17	13.63	13.52	13.18	13.03	104	0.88	2.64	No
ENDRIN	10	12.74	13.37	12.78	10.32	12.53	13.95	13.33	13.48	12.81	128	1.11	3.33	No
pp'-DDD	12.5	14.11	14.39	14.19	11.31	14.08	14.79	14.63	14.33	13.98	112	1.11	3.33	No
THIO-SS	10	11.29	11.73	11.72	8.79	11.31	11.83	11.75	11.74	11.27	113	1.02	3.06	No
pp'-DDT	12.5	10.72	10.90	10.82	8.44	10.79	11.42	11.33	10.88	10.66	85	0.93	2.79	No

*not detected

June 14, 1994
Determination of MDL values for OC/CB "B" compounds. Normal spiking levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
135-TCB	125	120.23	117.72	118.69	124.07	122.91	119.13	121.28	119.89	120.49	96	2.15	6.45	No
HCB	25	21.59	20.12	21.57	20.67	21.29	21.34	21.43	20.11	21.02	84	0.62	1.86	No
245-TCF	125	124.11	121.03	122.58	122.68	122.57	123.88	125.98	126.74	123.70	99	1.90	5.70	No
1245-TCB	25	26.33	25.06	24.72	24.94	25.39	25.59	25.64	28.13	25.72	103	1.09	3.27	Yes
CYCLOPENT	50	39.45	36.39	41.01	46.30	41.04	41.20	43.48	59.33	43.52	87	7.00	21.0	No
1234-TCB	25	26.14	26.86	26.19	26.58	26.38	26.57	27.22	27.99	26.74	107	0.62	1.86	No
HCB	25	25.49	24.74	25.20	25.24	24.93	25.05	24.95	24.99	25.07	100	0.23	0.69	No
LINDANE	25	25.55	23.95	24.64	25.04	24.43	25.05	25.23	24.96	24.86	99	0.50	1.50	No
ALDRIN	25	24.57	23.80	24.16	23.82	23.73	22.01	24.35	24.31	23.84	95	0.80	2.40	No
HEPTOXIDE	25	26.37	26.46	26.47	25.84	25.79	25.49	25.93	26.16	26.06	104	0.36	1.08	No
OCTA	25	23.96	22.71	23.50	23.22	23.23	22.65	23.57	23.58	23.30	93	0.45	1.35	No
THIODAN-1	50	50.02	50.39	50.33	48.64	49.54	48.24	49.28	49.35	49.47	99	0.77	2.31	No
pp'-DDE	125	124.74	124.86	124.65	120.51	120.96	113.02	119.50	122.40	121.33	97	3.95	11.85	No
ENDRIN	100	110.48	112.19	110.79	106.02	110.40	108.88	111.30	111.31	110.17	110	1.93	5.79	No
pp'-DDD	125	131.83	133.09	133.49	128.98	131.66	123.31	130.61	132.86	130.73	105	3.33	9.99	No
THIO-SS	100	105.36	107.45	106.46	99.95	102.85	103.81	104.49	106.23	104.58	105	2.39	7.17	No
pp'-DDT	125	130.23	128.21	132.35	124.12	130.63	116.99	128.41	129.33	127.53	102	4.89	14.67	Yes

July 6, 1994
Determination of MDL values for OC/CB "A" compounds. Normal spiking levels.

Compound	Spiked conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	ave. % rec.	std. dev. (ng/L)	est. MDL (ng/L)	Accept MDL ?
		1	2	3	4	5	6	7	8					
HCE	25	23.79	24.89	24.31	23.04	24.80	23.94	23.39	23.26	23.93	96	0.69	2.08	No
124-TCB	125	126.10	122.21	122.25	126.25	121.46	125.70	127.10	125.74	124.60	100	2.23	6.69	No
123-TCB	125	125.26	124.29	123.83	124.82	122.63	124.25	126.73	124.21	124.50	100	1.18	3.55	No
236-TCT	125	122.55	126.03	123.28	125.45	121.96	123.85	124.80	123.48	123.93	99	1.41	4.23	No
1235-TCB	25	25.19	25.89	25.25	26.29	24.35	25.29	24.92	24.75	25.24	101	0.62	1.85	No
26 α -TCT	125	125.20	125.25	124.95	125.12	124.51	123.38	125.70	125.68	124.97	100	0.75	2.25	No
PENTA	25	23.53	23.48	23.32	22.89	24.23	23.88	23.82	23.16	23.54	94	0.43	1.28	No
TRIFLURALIN	125	123.99	123.35	119.99	123.69	126.29	126.73	125.71	125.14	124.11	99	2.76	8.29	No
α -BHC	25	20.08	20.89	19.32	19.96	20.07	19.10	19.13	20.19	19.84	79	0.62	1.85	No
HEPTACHLOR	25	24.16	24.71	22.68	24.36	23.64	24.46	24.95	24.25	24.15	97	0.71	2.13	No
OXYCHLOR	50	49.46	49.39	46.25	48.79	47.98	49.33	50.23	49.35	48.85	98	1.23	3.69	No
γ -CHLORDAN	50	49.80	49.52	45.85	48.61	47.80	49.51	50.30	49.57	48.87	98	1.44	4.33	No
α -CHLORDAN	50	49.85	49.72	46.46	48.85	47.88	49.62	50.43	49.82	49.08	98	1.31	3.93	No
DIELDRIN	50	51.72	51.96	50.70	51.20	49.97	50.64	51.42	53.04	51.33	103	0.94	2.83	No
op' -DDT	125	124.46	124.36	112.36	119.77	115.89	121.28	123.50	121.83	120.43	96	4.31	12.90	Yes
THIODAN-2	100	99.48	104.00	104.01	104.06	97.63	100.63	102.50	106.33	102.33	102	2.87	8.62	No
MIREX	125	102.07	115.85	104.48	107.95	102.04	107.77	107.35	106.13	106.71	85	4.40	13.20	Yes
METHOXY	125	130.06	132.56	129.06	129.81	124.91	125.81	127.72	133.82	129.22	103	3.07	9.20	No

APPENDIX 3:

RECOVERY OF OC/CB COMPOUNDS

SPIKED IN REAL WATERS:

HEXANE MICRO-EXTRACTION

AND

METHOD OWOC-E3120B

February 10, 1994:

Recovery of OC/CB "B" compounds spiked into Lakeview treated water. Hexane micro-extraction.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)										ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9	10				
135-TCB	25	121.18	112.77	117.87	117.75	116.20	121.53	139.18	116.34	119.31	119.24	120.20	7.18	96	6
HCBD	125	20.94	17.79	19.29	17.52	18.82	19.34	21.12	18.69	18.88	17.15	18.95	1.32	76	5
245-TCT	125	128.12	119.92	124.84	126.33	123.25	126.22	138.17	122.89	123.79	123.16	125.67	4.95	101	4
1245-TCB	125	27.38	24.02	25.21	25.94	24.89	25.33	27.07	25.51	23.66	25.24	25.43	1.17	102	5
CYCLOPENT	25	52.50	170.89	175.16	194.33	149.20	181.27	219.08	47.45	125.52	23.39	INT*			
1234-TCB	125	27.25	24.66	25.41	25.73	25.08	25.75	26.97	25.53	27.24	25.72	25.93	0.91	104	4
HCB	25	27.00	25.96	26.54	28.78	27.61	28.75	21.93	28.57	28.03	27.22	27.04	2.03	108	8
LINDANE	125	20.94	19.48	19.40	20.75	20.10	20.83	15.44	20.63	20.49	20.20	19.83	1.53	79	7
ALDRIN	25	24.12	21.52	24.04	23.68	23.46	24.60	17.23	23.16	23.33	22.29	22.74	2.14	91	9
HEPTOXIDE	25	29.69	25.57	27.45	28.84	27.77	29.05	20.40	28.08	28.27	27.41	27.25	2.66	109	11
OCTA	50	27.50	22.54	25.03	26.57	24.78	26.11	18.45	24.68	24.84	23.81	24.43	2.52	98	10
THIODAN-1	50	57.81	49.38	55.11	56.56	53.85	56.87	39.98	55.94	55.48	53.45	53.44	5.29	107	11
pp'-DDE	50	146.75	131.56	138.19	152.50	143.35	154.93	107.20	143.89	150.36	139.81	140.85	13.75	113	11
ENDRIN	50	131.00	109.82	120.02	128.95	121.20	128.22	85.62	116.74	122.66	113.56	117.78	13.19	118	13
pp'-DDD	125	139.94	124.51	134.46	149.65	139.57	143.46	102.12	136.51	145.03	132.32	134.76	13.47	108	11
THIO-SS	100	105.00	98.70	106.84	115.72	109.78	117.36	80.50	105.94	113.62	103.68	105.72	10.56	106	10
pp'-DDT	125	140.81	133.52	137.49	142.76	144.78	152.30	99.68	133.75	142.57	130.46	135.81	14.21	109	11

* coextracted compound interfered with analysis.

March 22, 1994:
Recovery of OC/CB "B" compounds spiked into Lakeview raw water. Hexane micro-extraction.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)									ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9				
135-TCB	125	117.48	111.88	113.17	114.89	115.44	115.85	114.07	112.96	112.35	114.23	1.83	91	1
HCB	25	20.16	17.95	18.95	19.69	19.67	20.21	18.70	18.44	18.36	19.13	0.83	77	3
245-TCT	125	121.56	115.93	116.15	119.43	119.28	119.00	117.70	116.63	115.40	117.90	2.05	94	2
1245-TCB	25	25.44	24.17	24.06	25.36	24.65	24.69	24.91	24.40	n/a	24.71	0.51	99	2
CYCLOPENT	50	37.89	33.77	34.80	36.62	38.61	36.65	35.56	33.83	36.36	36.01	1.68	72	3
1234-TCB	25	26.13	24.82	25.04	24.77	24.82	24.70	24.61	24.64	26.17	25.08	0.62	100	2
HCB	25	25.82	24.80	24.98	24.92	24.81	24.65	24.50	24.75	24.81	24.89	0.37	100	2
LINDANE	25	26.14	25.02	24.88	24.47	24.84	24.61	24.63	24.42	24.71	24.86	0.52	99	2
ALDRIN	25	26.10	24.58	24.64	25.50	25.07	24.89	23.82	23.37	23.78	24.64	0.88	99	4
HEPTOXIDE	25	27.94	26.89	27.34	27.22	27.15	26.87	26.74	25.75	26.43	26.93	0.61	108	2
OCTA	25	24.98	23.67	23.51	24.36	23.96	23.81	22.84	22.18	22.85	23.57	0.85	94	3
THIODAN-1	50	55.64	52.81	53.98	53.28	52.99	52.55	52.76	50.34	52.11	52.94	1.42	106	3
pp'-DDE	125	134.17	129.15	130.28	130.28	130.30	128.44	127.57	123.49	127.95	129.07	2.86	103	2
ENDRIN	100	122.35	118.21	118.98	123.01	116.63	115.45	115.83	113.31	114.81	117.62	3.34	118	3
pp'-DDD	125	139.10	133.58	135.84	134.07	134.82	132.27	132.99	126.12	132.75	133.50	3.46	107	3
THIO-SS	100	113.93	109.82	111.80	109.36	110.06	108.47	109.12	102.67	107.63	109.21	3.08	109	3
pp'-DDT	125	136.58	131.51	132.42	130.96	131.93	128.11	128.85	121.88	129.12	130.15	3.99	104	3

March 31, 1994:

Recovery of OC/CB "A" compounds spiked into Verner raw water.Hexane micro-extraction.

156

Compound	Spiking conc. (ng/L)	Recovery (ng/L)										ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9	10				
HCE	25	24.10	21.98	21.43	22.45	24.47	24.43	23.32	21.58	22.27	21.57	22.76	1.22	91	5
124-TCB	125	129.0	128.84	122.64	124.04	130.03	130.19	126.84	124.88	129.21	126.04	127.17	2.68	102	2
123-TCB	125	130.8	129.38	123.93	125.49	132.14	130.47	126.43	126.15	130.74	127.73	128.33	2.75	103	2
236-TCT	125	118.36	117.97	116.40	118.42	123.49	120.38	119.24	114.13	120.22	117.83	118.64	2.49	95	2
1235-TCB	25	24.02	25.79	24.28	23.85	24.68	24.55	24.39	23.51	24.72	23.65	24.34	0.66	97	3
26 α -TCT	125	132.12	129.74	129.69	126.64	132.86	132.07	129.48	128.53	132.32	130.58	130.40	1.97	104	2
PENTA	25	22.88	23.49	22.62	21.92	21.86	22.66	21.06	22.71	24.15	22.79	22.61	0.86	90	3
TRIFLURALIN	125	127.86	124.11	129.86	125.54	122.01	122.65	121.33	121.98	134.77	128.49	125.86	4.35	101	3
α -BHC	25	26.17	24.88	24.87	24.96	25.88	25.86	24.95	25.01	25.70	25.16	25.34	0.50	101	2
HEPTACHLOR	25	20.60	19.73	21.44	19.99	19.43	19.61	19.59	18.82	21.21	20.20	20.06	0.82	80	3
OXYCHLOR	50	43.62	41.99	44.04	42.08	40.95	39.89	40.64	39.86	45.80	42.75	42.16	1.93	84	4
γ -CHLORDAN	50	40.46	39.26	39.77	37.46	36.36	35.60	36.38	35.31	41.57	37.65	37.98	2.17	76	4
α -CHLORDAN	50	40.74	39.72	40.61	38.85	37.47	36.81	37.70	36.83	42.12	38.67	38.95	1.81	78	4
DIELDRIN	50	49.76	48.58	50.04	49.58	48.02	47.87	48.20	48.53	51.89	50.33	49.28	1.27	99	3
op'-DDT	125	79.03	80.66	75.65	70.31	62.69	66.29	70.38	65.36	78.83	68.21	71.74	6.39	57	5
THIODAN-2	100	104.81	101.76	102.09	101.88	102.89	102.60	101.40	101.15	106.34	103.88	102.88	1.66	103	2
MIREX	125	32.23	36.62	28.61	29.36	26.82	31.34	35.30	31.04	36.93	33.18	32.14	3.41	26	3
METHOXY	125	119.20	119.02	120.74	117.57	112.28	114.01	119.93	114.57	129.20	118.50	118.30	4.66	95	4

March 31, 1994:

Recovery of OC/CB "A" compounds spiked into Verner treated water. Hexane micro-extraction.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)										ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9	10				
HCE	25	22.82	23.43	23.24	24.22	23.70	22.62	24.14	23.58	22.34	23.41	23.35	0.62	93	2
124-TCB	125	115.79	120.19	117.34	119.18	117.02	116.63	119.20	118.59	115.50	117.78	117.72	1.56	94	1
123-TCB	125	123.17	128.13	123.42	126.85	123.44	122.62	123.88	123.38	122.46	124.73	124.21	1.86	99	1
236-TCF	125	114.60	113.99	115.13	120.22	117.87	117.96	117.80	117.53	115.02	120.08	117.02	2.23	94	2
1235-TCB	25	24.10	24.08	24.02	26.91	26.15	26.43	24.20	24.28	23.55	24.33	24.80	1.20	99	1
26 α -TCF	125	128.76	132.23	132.85	136.31	135.42	132.24	137.30	133.98	126.34	127.05	132.25	3.79	106	3
PENTA	25	25.96	26.05	24.76	25.74	23.22	25.03	23.08	25.55	25.68	25.60	25.07	1.08	100	4
TRIFLURALIN	125	122.93	123.26	125.98	128.38	129.02	129.67	130.61	127.95	131.81	132.06	128.17	3.23	102	3
α -BHC	25	24.71	24.37	25.13	25.22	25.10	24.99	25.34	25.25	25.12	24.98	25.02	0.29	100	1
HEPTACHLOR	25	21.79	21.38	22.49	23.01	22.87	22.36	23.25	22.34	22.02	21.92	22.34	0.59	89	2
OXYCHLOR	50	52.69	52.11	53.72	55.09	54.69	51.94	55.64	51.22	51.34	50.56	52.90	1.78	106	4
γ -CHLORDAN	50	51.20	50.11	51.47	52.36	51.71	51.99	51.50	51.40	52.43	51.06	51.52	0.68	103	1
α -CHLORDAN	50	51.16	50.04	51.30	51.97	51.06	51.57	50.89	50.48	51.61	50.61	51.07	0.58	102	1
DIELDRIN	50	55.42	55.20	56.85	57.89	58.08	54.58	59.90	54.10	52.77	52.85	55.76	2.36	112	5
op' -DDT	125	134.18	131.93	137.24	140.29	139.66	129.99	140.50	128.12	129.10	125.84	133.68	5.47	107	4
THIODAN-2	100	108.31	107.77	106.42	111.87	109.02	106.32	108.04	107.02	106.50	108.14	107.94	1.66	108	2
MIREX	125	90.45	83.78	86.28	86.14	87.09	82.69	90.48	69.58	82.76	86.19	84.54	5.93	68	5
METHOXY	125	141.45	142.03	148.89	153.67	153.22	138.67	158.05	138.97	129.09	129.78	143.38	9.91	115	8

March 31, 1994:

Recovery of OC/CB "B" compounds spiked into Verner raw water. Hexane micro-extraction.

Compound		Spiking conc. (ng/L)	Recovery (ng/L)									ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
			1	2	3	4	5	6	7	8	9				
135-TCB	25	111.60	108.86	112.02	101.69	113.96	112.12	116.30	112.38	113.12	111.34	4.13	89	3	
HCBD	125	15.40	15.05	15.45	12.92	16.27	16.54	16.96	15.93	15.86	15.60	1.17	62	5	
245-TCT	125	114.32	114.06	116.15	108.49	115.75	117.02	118.54	116.21	115.69	115.14	2.83	92	2	
1245-TCB	125	26.09	26.61	26.82	25.71	26.29	27.16	27.18	27.08	26.70	26.63	0.51	107	2	
CYCLOPENT	25	63.65	109.30	309.70	892	580	927	908	710	780	int.	int.			
1234-TCB	125	25.85	25.64	26.71	26.71	26.28	27.37	26.02	26.24	27.03	26.43	0.57	106	2	
HCB	25	27.45	27.39	27.31	27.84	26.94	26.64	26.62	26.23	26.33	26.97	0.56	108	2	
LINDANE	125	25.85	25.31	24.85	24.58	24.78	24.57	23.96	23.76	24.76	24.71	0.63	99	3	
ALDRIN	25	17.41	16.97	16.13	15.88	17.17	16.66	15.88	16.78	15.84	16.52	0.61	66	2	
HEPTOXIDE	25	25.77	24.76	24.88	24.10	25.36	24.14	24.33	25.06	24.66	24.78	0.56	99	2	
OCTA	50	13.08	13.02	11.66	11.66	12.86	11.92	11.10	11.88	10.35	11.95	0.92	48	4	
THIODAN-1	50	50.04	48.57	48.50	48.02	48.90	47.30	47.40	49.45	48.50	48.52	0.89	97	2	
pp'-DDE	50	75.92	76.08	68.11	72.11	72.04	70.28	66.86	71.89	65.32	70.96	3.73	57	3	
ENDRIN	100	108.95	106.48	106.33	106.98	108.00	105.44	105.42	110.99	107.25	107.32	1.79	107	2	
pp'-DDD	125	103.08	97.24	96.73	97.76	98.96	97.28	96.34	104.57	98.46	98.94	2.91	79	2	
THIO-SS	100	95.34	94.42	92.81	90.17	93.33	90.00	90.26	91.89	90.37	92.07	2.01	92	2	
pp'-DDT	125	80.54	81.65	72.26	76.33	76.62	74.76	71.19	78.13	69.26	75.64	4.19	61	3	

March 31, 1994:

Recovery of OC/CB "B" compounds spiked into Verner treated water. Hexane micro-extraction.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)									ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9				
135-TCB	25	111.26	112.18	107.44	110.25	117.39	105.23	107.21	103.68	99.11	108.20	5.33	87	4
HCBD	125	15.55	14.08	14.16	14.51	16.56	13.30	13.77	13.40	12.50	14.20	1.23	57	5
245-TCT	125	117.99	117.07	114.64	116.34	120.06	110.99	111.70	108.83	107.09	113.86	4.42	91	4
1245-TCB	125	26.91	26.89	26.17	26.46	27.09	25.50	25.74	25.32	24.84	26.10	0.80	104	3
CYCLOPENT	25	88.50	89.70	88.93	90.20	95.71	105.50	126.20	222.46	202.6	int.	int.		
1234-TCB	125	27.06	27.98	26.18	26.85	26.82	25.84	26.00	26.01	25.56	26.48	0.76	106	3
HCB	25	30.31	30.62	29.32	31.63	29.33	29.62	28.26	28.58	28.19	29.54	1.15	118	5
LINDANE	125	29.44	29.22	28.64	28.84	28.73	28.56	28.20	28.05	28.16	28.65	0.47	115	2
ALDRIN	25	22.42	22.54	21.85	21.94	21.70	22.01	21.02	19.97	20.76	21.58	0.84	86	3
HEPTOXIDE	25	25.99	27.35	26.76	27.12	26.39	26.69	26.10	25.94	26.04	26.49	0.52	106	2
OCTA	50	19.99	20.35	19.40	19.51	17.92	19.82	18.62	17.66	17.86	19.01	1.02	76	4
THIODAN-1	50	50.40	53.40	52.25	53.11	52.08	52.10	50.98	51.20	50.91	51.83	1.03	104	2
pp'-DDE	50	113.08	121.38	115.50	116.33	109.79	119.35	112.58	110.80	112.31	114.57	3.90	92	3
ENDRIN	100	114.70	124.10	121.09	125.49	122.97	123.66	120.34	121.14	120.79	121.59	3.12	122	3
pp'-DDD	125	114.72	124.92	125.66	127.24	123.93	132.24	129.18	128.91	128.75	126.17	4.99	101	4
THIO-SS	100	91.51	99.15	96.52	99.38	98.36	98.82	95.15	94.36	95.30	96.51	2.67	97	3
pp'-DDT	125	122.38	132.70	129.41	130.44	122.26	133.68	125.30	123.56	127.11	127.43	4.35	102	3

April 20, 1994:

Recovery of OC/CB "A" compounds spiked into Lakeview raw water. Hexane micro-extraction.

160

Compound	Spiking conc. (ng/L)	Recovery (ng/L)										ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9	10				
HCE	25	21.93	24.66	23.65	24.07	23.97	22.74	23.22	23.30	22.18	21.01	23.07	1.11	92	4
124-TCB	125	117.61	117.88	123.50	121.78	122.76	121.02	122.14	120.25	119.82	116.00	120.28	2.45	96	2
123-TCB	125	116.90	118.48	122.90	121.53	129.19	121.50	122.86	120.04	120.47	118.99	121.29	3.37	97	3
236-TCT	125	118.93	119.25	121.28	119.28	121.60	116.01	118.85	119.63	117.32	116.34	118.85	1.86	95	1
1235-TCB	25	24.65	24.98	25.24	24.85	25.19	23.84	24.67	24.58	24.58	24.36	24.69	0.41	99	2
26 α -TCT	125	120.48	124.29	125.90	127.44	123.79	126.80	127.90	121.92	122.90	123.03	124.45	2.5	100	2
PENTA	25	24.25	24.63	25.92	27.42	24.20	28.17	24.76	23.38	23.54	23.34	24.96	1.7	100	7
TRIFLURALIN	125	170.35	170.37	177.95	188.70	168.71	175.43	178.93	169.73	172.51	169.58	174.22	6.26	139	5
α -BHC	25	23.72	24.42	24.17	24.98	24.64	25.14	25.84	24.93	24.52	24.89	24.73	0.6	99	2
HEPTACHLOR	25	25.01	24.85	24.79	26.08	24.54	26.34	25.36	24.93	25.40	24.93	25.22	0.6	101	2
OXYCHLOR	50	50.82	50.70	49.79	51.81	50.18	54.47	51.64	50.77	52.55	51.38	51.41	1.34	103	3
γ -CHLORDAN	50	51.23	50.37	49.04	51.01	49.98	51.34	51.14	50.66	52.64	51.69	50.91	0.98	102	2
α -CHLORDAN	50	50.49	50.11	49.02	51.27	49.61	54.65	51.45	50.48	52.65	51.31	51.10	1.62	102	3
DIELDRIN	50	51.40	50.82	50.70	53.02	50.85	55.70	52.94	51.03	53.56	51.50	52.15	1.63	104	3
op' -DDT	125	129.02	127.85	122.35	132.05	125.33	129.29	128.77	126.83	136.84	130.85	128.92	3.9	103	3
THIODAN-2	100	100.97	100.47	96.61	101.87	98.49	103.25	103.16	100.62	105.74	102.08	101.33	2.56	101	3
MIREX	125	116.17	118.22	109.72	120.33	111.84	120.47	126.32	113.42	129.09	121.28	118.69	6.2	95	5
METHOXY	125	135.49	133.88	126.66	136.89	127.94	134.82	141.04	130.33	157.42	137.67	136.21	8.7	109	7

April 20, 1994:

Recovery of OC/CB "A" compounds spiked into Lakeview treated water. Hexane micro-extraction.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)										ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9	10				
HCE	25	24.03	26.57	25.79	26.54	26.41	26.85	27.39	27.06	27.28	27.60	26.55	1.03	106	4
124-TCB	125	123.49	120.55	120.78	121.90	119.91	120.14	121.50	125.40	122.67	122.93	121.93	1.72	98	1
123-TCB	125	121.30	117.53	119.51	119.15	119.13	119.23	121.32	122.54	119.83	119.35	119.89	1.44	96	1
236-TCT	125	120.90	117.23	117.12	118.94	118.22	119.44	120.93	121.03	120.30	119.94	119.40	1.48	96	1
1235-TCB	25	25.51	24.99	24.82	25.06	24.59	24.41	25.23	25.84	24.76	24.44	24.96	0.46	100	2
26 α -TCT	125	125.98	124.71	126.84	125.50	126.10	123.18	125.73	129.28	124.00	125.61	125.69	1.65	101	1
PENTA	25	24.10	23.90	23.75	23.66	23.60	23.73	26.45	27.57	24.15	24.48	24.54	1.36	98	5
TRIFLURALIN	125	178.49	172.33	180.65	173.99	177.90	182.87	185.82	200.65	182.34	184.87	181.99	7.89	146	6
α -BHC	25	25.29	25.20	25.52	25.31	25.73	24.45	24.77	25.45	24.52	24.98	25.12	0.43	100	2
HEPTACHLOR	25	26.19	25.47	26.56	25.85	26.24	25.65	25.86	27.35	25.82	25.83	26.08	0.54	104	2
OXYCHLOR	50	52.12	51.14	43.76	52.18	53.64	51.28	51.65	53.25	51.30	51.57	52.19	1.01	104	2
γ -CHLORDAN	50	52.31	51.63	43.96	52.03	53.67	51.28	51.91	53.34	51.29	51.87	52.33	0.98	105	2
α -CHLORDAN	50	51.49	51.46	53.54	51.78	53.25	51.05	51.52	53.40	51.02	52.06	52.06	0.98	104	2
DIELDRIN	50	52.82	52.26	54.13	52.41	53.97	51.55	52.01	54.85	51.98	52.44	52.84	1.09	106	2
op'-DDT	125	134.08	133.93	141.23	135.77	140.29	133.30	135.91	138.53	135.53	136.56	136.51	2.70	109	2
THIODAN-2	100	101.30	102.34	105.88	101.73	105.34	100.43	104.24	108.03	104.22	104.83	103.83	2.36	104	2
MIREX	125	105.56	106.36	116.78	110.63	112.80	108.50	117.20	118.18	114.80	114.64	112.54	4.57	90	4
METHOXY	125	132.78	138.45	142.14	135.36	142.50	135.00	140.78	145.80	140.98	143.29	139.71	4.18	112	3

June 14, 1994: Comparison of methods.
 Recovery of OC/CB "B" compounds spiked into HPLC grade water. Method OWOC-E3120.
 Internal standard quantitation.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
135-TCB	125	109.02	119.16	106.12	109.16	109.69	108.20	112.11	111.51	110.62	3.92	88	3
HCBD	25	16.46	19.23	15.29	16.53	17.00	16.74	17.25	16.97	16.93	1.10	68	4
245-TCT	125	120.85	125.20	119.61	116.68	120.11	114.65	120.93	121.78	119.98	3.20	96	3
1245-TCB	25	24.60	23.43	24.42	22.95	23.30	22.22	23.16	23.16	23.40	0.77	94	3
CYCLOPENT	50	28.54	X	X	24.83	21.95	21.27	X	23.89	24.10	2.87	48	6
1234-TCB	25	27.34	30.02	29.44	28.69	27.37	27.29	26.89	27.34	28.05	1.17	112	5
HCB	25	25.23	26.35	26.34	25.06	25.19	24.26	25.26	24.46	25.27	0.76	101	3
LINDANE	25	26.54	24.51	26.19	25.89	26.08	26.25	25.57	25.10	25.77	0.67	103	3
ALDRIN	25	23.52	23.63	22.35	23.54	23.63	22.15	23.19	22.90	23.11	0.59	92	2
HEPTOXIDE	25	26.13	25.27	26.32	25.41	25.75	25.22	25.07	24.90	25.51	0.51	102	2
OCTA	25	21.76	23.86	21.70	22.79	22.27	21.40	22.05	21.52	22.17	0.82	89	3
THIODAN-1	50	49.80	49.58	50.86	49.11	49.62	49.97	47.36	46.47	49.10	1.45	98	3
pp'-DDE	125	119.53	116.85	119.77	117.15	118.20	119.48	115.37	113.35	117.46	2.27	94	2
ENDRIN	100	110.13	106.62	107.31	108.78	109.31	109.53	105.78	107.69	108.14	1.53	108	2
pp'-DDD	125	125.89	123.62	126.28	124.34	125.13	127.10	122.62	120.96	124.49	2.04	100	2
THIO-SS	100	97.44	105.89	91.52	96.34	96.57	96.61	93.47	92.87	96.34	4.41	96	4
pp'-DDT	125	130.52	105.26	116.71	126.15	128.54	127.49	123.65	122.42	122.59	8.20	98	7

June 14, 1994: Comparison of methods.

Recovery of OC/CB "B" compounds spiked into HPLC grade water. Hexane micro-extraction. Quantitation by internal standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
135-TCB	125	120.23	117.72	118.69	124.07	122.91	119.13	121.28	119.89	120.49	2.15	96	2
HCBD	25	21.59	20.12	21.57	20.67	21.29	21.34	21.43	20.11	21.02	0.62	94	2
245-TCT	125	124.11	121.03	122.58	122.68	122.57	123.88	125.98	126.74	123.70	1.90	99	2
1245-TCB	25	26.33	25.06	24.72	24.94	25.39	25.59	25.64	28.13	25.72	1.09	103	4
CYCLOPENT	50	39.45	36.39	41.01	46.30	41.04	41.20	43.48	59.33	43.52	7.00	87	14
1234-TCB	25	26.14	26.86	26.19	26.58	26.38	26.57	27.22	27.99	26.74	0.62	107	2
HCB	25	25.49	24.74	25.20	25.24	24.93	25.05	24.95	24.99	25.07	0.23	100	1
LINDANE	25	25.55	23.95	24.64	25.04	24.43	25.05	25.23	24.96	24.86	0.50	99	2
ALDRIN	25	24.57	23.80	24.16	23.82	23.73	22.01	24.35	24.31	23.84	0.80	95	3
HEPTOXIDE	25	26.37	26.46	26.47	25.84	25.79	25.49	25.93	26.16	26.06	0.36	104	1
OCTA	25	23.96	22.71	23.50	23.22	23.23	22.65	23.57	23.58	23.30	0.45	93	2
THIODAN-1	50	50.02	50.39	50.33	48.64	49.54	48.24	49.28	49.35	49.47	0.77	99	2
pp'-DDE	125	124.74	124.86	124.65	120.51	120.96	113.02	119.50	122.40	121.33	3.95	97	3
ENDRIN	100	110.48	112.19	110.79	106.02	110.40	108.88	111.30	111.31	110.17	1.93	110	2
pp'-DDD	125	131.83	133.09	133.49	128.98	131.66	123.31	130.61	132.86	130.73	3.33	105	3
THIO-SS	100	105.36	107.45	106.46	99.95	102.85	103.81	104.49	106.23	104.58	2.39	105	2
pp'-DDT	125	130.23	128.21	132.35	124.12	130.63	116.99	128.41	129.33	127.53	4.89	102	4

July 7, 1994: Comparison of methods.
 Recovery of OC/CB "A" compounds spiked into HPLC grade water. Method OMOC-E3120B.
 Quantitation by external standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
HCE	25	19.52	19.72	20.80	19.41	20.33	23.59	18.14	19.21	20.09	1.62	80	6
124-TCB	125	122.53	128.16	134.16	123.96	126.46	155.13	116.26	121.99	128.58	11.92	103	10
123-TCB	125	129.55	131.25	139.73	128.76	131.38	158.95	120.71	125.51	133.23	11.72	107	9
236-TCT	125	124.82	127.63	131.13	118.94	128.71	146.13	111.51	117.69	125.82	10.50	101	8
1235-TCB	25	26.52	26.09	27.29	25.86	26.98	31.03	22.95	24.55	26.41	2.34	106	9
26 α -TCT	125	138.45	139.08	154.47	138.94	140.83	163.67	131.66	135.94	142.88	10.65	114	9
PENTA	25	25.26	25.74	27.63	25.84	27.85	29.32	23.08	22.98	25.96	2.25	104	9
TRIFLURALIN	125	123.67	121.71	137.59	124.26	128.62	141.89	117.31	123.27	127.29	8.37	102	7
α -BHC	25	21.68	22.09	23.90	21.84	22.34	25.14	21.13	21.49	22.45	1.37	90	5
HEPTACHLOR	25	25.76	26.63	27.44	26.08	26.73	29.66	24.54	24.76	26.45	1.53	106	6
OXYCHLOR	50	51.10	52.51	56.53	51.56	51.71	58.42	49.77	50.26	52.73	3.09	105	6
γ -CHLORDAN	50	51.12	52.75	56.88	51.65	51.71	58.70	50.33	50.23	52.92	3.15	106	6
α -CHLORDAN	50	51.22	52.54	56.82	51.43	51.44	58.41	50.19	49.97	52.75	3.13	106	6
DIELDRIN	50	51.90	54.14	58.63	52.80	52.63	60.57	52.81	52.14	54.45	3.29	109	7
op' -DDT	125	127.64	132.96	145.04	129.48	129.71	148.09	127.57	126.51	133.38	8.41	107	7
THIODAN-2	100	103.09	106.85	115.30	103.59	104.07	118.34	102.59	101.73	106.94	6.33	107	6
MIREX	125	115.54	122.29	140.60	127.56	120.78	138.72	126.45	123.77	126.96	8.66	102	7
METHOXY	125	130.60	135.89	148.68	135.69	137.26	158.69	136.71	133.07	139.57	9.36	112	7
135-TBB (surrogate)	125	130.92	132.20	144.00	130.89	133.27	152.77	121.44	125.06	133.82	10.09	107	8

July 7, 1994: Comparison of methods.
Recovery of OC/CB "A" compounds spiked into HPLC grade water. Method OWOC-E3120B.
Quantitation by internal standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
HCE	25	18.77	18.69	18.45	18.25	18.97	19.16	18.29	19.27	18.73	0.38	75	2
124-TCB	125	116.95	121.16	118.68	114.35	114.53	122.39	115.55	117.56	117.65	2.96	94	2
123-TCB	125	123.68	124.09	123.63	122.44	122.68	129.44	123.74	124.86	124.32	2.20	99	2
236-TCT	125	119.16	120.68	116.02	111.61	118.59	117.44	112.75	115.54	116.47	3.14	93	3
1235-TCB	25	25.31	24.67	24.59	23.31	23.96	24.00	22.31	23.18	23.92	0.96	96	4
26 α -TCT	125	132.18	131.51	133.87	128.36	127.77	129.53	131.12	131.44	130.72	2.04	105	2
PENTA	25	24.12	24.34	23.66	25.59	24.81	24.89	24.64	23.83	24.48	0.63	98	3
TRIFLURALIN	125	118.06	112.76	121.74	116.33	116.97	112.80	117.33	121.64	117.20	3.40	94	3
α -BHC	25	20.70	20.89	21.14	21.20	21.28	20.92	22.12	21.85	21.26	0.49	85	2
HEPTACHLOR	25	24.59	25.18	24.27	23.40	23.55	22.80	23.73	23.25	23.85	0.78	95	3
OXYCHLOR	50	48.78	49.65	50.05	48.36	47.63	46.94	50.31	49.35	48.88	1.18	98	2
γ -CHLORDAN	50	48.98	49.88	50.33	48.78	47.96	47.51	51.24	49.66	49.29	1.23	99	2
α -CHLORDAN	50	48.9	49.68	50.28	48.35	47.49	47.06	50.86	49.18	48.98	1.31	98	3
DIELDRIN	50	49.56	51.20	50.88	48.77	47.75	47.94	52.58	50.41	49.89	1.69	100	3
op' -DDT	125	121.88	125.72	128.35	119.84	117.91	117.44	127.23	122.59	122.62	4.16	98	3
THIODAN-2	100	98.43	101.03	102.02	96.97	95.67	94.91	103.50	99.70	99.03	3.08	99	3
MIREX	125	110.34	115.64	124.42	119.39	111.05	111.26	127.55	121.30	117.62	6.57	94	5
METHOXY	125	124.68	128.49	131.55	118.52	117.70	118.70	128.73	121.59	123.74	5.39	99	4

July 7, 1994: Comparison of methods.
 Recovery of OC/CB "A" compounds spiked into HPLC grade water. Hexane micro-extraction.
 External standard quantitation.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
HCE	25	28.64	27.46	26.10	25.67	27.67	25.39	25.39	26.54	26.61	1.20	106	5
124-TCB	125	151.79	134.91	131.22	140.62	135.42	133.33	137.94	143.47	138.59	6.64	111	5
123-TCB	125	150.79	137.19	132.94	139.08	136.74	131.80	137.52	141.71	138.47	5.89	111	5
236-TCT	125	147.56	139.12	132.33	139.79	136.01	131.40	135.47	140.89	137.82	5.21	110	4
1235-TCB	25	30.33	28.58	27.11	29.28	27.15	26.84	27.06	28.25	28.08	1.26	112	5
26 α -TCT	125	150.74	138.27	134.13	139.46	138.27	130.90	136.46	143.40	138.95	6.03	111	5
PENTA	25	28.31	25.91	25.04	25.48	27.01	25.34	25.83	26.40	26.16	1.07	105	4
TRIFLURALIN	125	149.26	136.16	126.65	137.84	140.84	134.44	136.41	142.78	138.05	6.60	110	5
α -BHC	25	24.19	23.06	20.74	22.25	22.38	20.26	20.76	23.05	22.09	1.38	88	6
HEPTACHLOR	25	29.09	27.27	24.35	27.15	26.36	25.95	27.08	27.67	26.86	1.38	107	6
OXYCHLOR	50	59.55	54.52	49.64	54.37	53.50	52.33	54.52	56.31	54.34	2.88	109	6
γ -CHLORDAN	50	59.96	54.67	49.22	54.17	53.30	52.53	54.60	56.56	54.00	2.44	108	5
α -CHLORDAN	50	60.01	54.88	49.87	54.46	53.39	52.64	54.73	56.85	54.60	2.98	109	6
DIELDRIN	50	62.27	57.36	54.43	57.06	55.72	53.77	55.81	60.51	57.12	2.93	114	6
op'-DDT	125	149.83	137.28	120.61	133.49	129.22	128.68	134.54	139.02	134.08	8.60	107	7
THIODAN-2	100	119.77	114.81	111.65	115.97	108.86	106.76	111.24	121.32	113.80	5.11	114	5
MIREX	125	122.89	127.89	112.16	120.30	113.77	114.34	116.52	121.10	118.62	5.36	95	4
METHOXY	125	156.57	146.31	138.55	144.67	139.27	133.48	138.63	152.69	143.76	7.83	115	6
135-TBB (surrogate)	125	150.50	138.00	134.18	139.32	139.38	132.62	135.70	142.64	139.04	5.63	111	4

July 7, 1994: Comparison of methods.
Recovery of OC/CB "A" compounds spiked into HPLC grade water. Hexane micro-extraction.
Quantitation by internal standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
HCE	25	23.79	24.89	24.31	23.04	24.80	23.94	23.39	23.26	23.93	0.69	96	3
124-TCB	125	126.10	122.21	122.25	126.25	121.46	125.70	127.10	125.74	124.60	2.23	100	2
123-TCB	125	125.26	124.29	123.83	124.82	122.63	124.25	126.73	124.21	124.50	1.18	100	1
236-TCT	125	122.55	126.03	123.28	125.45	121.96	123.85	124.80	123.48	123.93	1.41	99	1
1235-TCB	25	25.19	25.89	25.25	26.29	24.35	25.29	24.92	24.75	25.24	0.62	101	2
26 α -TCT	125	125.20	125.25	124.95	125.12	124.51	123.38	125.70	125.68	124.97	0.75	100	1
PENTA	25	23.53	23.48	23.32	22.89	24.23	23.88	23.82	23.16	23.54	0.43	94	2
TRIFLURALIN	125	123.99	123.35	119.99	123.69	126.29	126.73	125.71	125.14	124.11	2.76	99	2
α -BHC	25	20.08	20.89	19.32	19.96	20.07	19.10	19.13	20.19	19.84	0.62	79	2
HEPTACHLOR	25	24.16	24.71	22.68	24.36	23.64	24.46	24.95	24.25	24.15	0.71	97	3
OXYCHLOR	50	49.46	49.39	46.25	48.79	47.98	49.33	50.23	49.35	48.85	1.23	98	2
γ -CHLORDAN	50	49.80	49.52	45.85	48.61	47.80	49.51	50.30	49.57	48.87	1.44	98	3
α -CHLORDAN	50	49.85	49.72	46.46	48.85	47.88	49.62	50.43	49.82	49.08	1.31	98	3
DIELDRIN	50	51.72	51.96	50.70	51.20	49.97	50.64	51.42	53.04	51.33	0.94	103	2
op' -DDT	125	124.46	124.36	112.36	119.77	115.89	121.28	123.50	121.83	120.43	4.31	96	3
THIODAN-2	100	99.48	104.00	104.01	104.06	97.63	100.63	102.50	106.33	102.33	2.87	102	3
MIREX	125	102.07	115.85	104.48	107.95	102.04	107.77	107.35	106.13	106.71	4.40	85	3
METHOXY	125	130.06	132.56	129.06	129.81	124.91	125.81	127.72	133.82	129.22	3.07	103	2

July 7, 1994: Comparison of methods.
Recovery of OC/CB "A" compounds spiked into Verner raw water. Method OMOC-E3120B.
Quantitation by external standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)									ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9				
HCE	25	19.16	20.35	23.51	24.62	18.92	23.47	21.18	19.64	22.30	21.46	2.10	86	8
124-TCB	125	127.11	131.79	146.28	154.50	122.16	147.92	136.69	124.26	154.35	138.34	12.77	111	10
123-TCB	125	132.38	135.34	155.60	162.91	129.65	156.52	144.83	128.28	167.11	145.85	15.07	117	12
236-TCT	125	121.66	126.56	146.84	156.13	121.21	142.30	134.96	116.31	153.24	135.47	14.83	108	12
1235-TCB	25	26.47	27.15	32.04	33.87	26.20	30.52	28.84	25.20	31.27	29.06	3.01	116	12
26 α -TCT	125	140.04	139.54	161.62	172.54	138.24	168.49	151.24	136.07	180.15	154.21	16.89	123	14
PENTA	25	25.92	25.97	30.17	31.99	25.53	30.15	27.97	24.67	32.17	28.28	2.91	113	12
TRIFLURALIN	125	117.77	107.49	129.05	132.71	108.67	140.51	122.05	114.12	162.93	126.14	17.66	101	14
α -BHC	25	22.97	22.66	26.28	27.59	22.70	27.26	24.50	21.72	30.05	25.08	2.85	100	11
HEPTACHLOR	25	24.70	23.67	27.76	28.83	24.84	28.98	25.54	23.60	32.28	26.69	2.95	107	12
OXYCHLOR	50	49.76	45.89	54.09	56.90	47.33	58.08	49.84	47.63	63.14	52.52	5.86	105	12
γ -CHLORDAN	50	50.60	45.14	54.01	56.87	47.64	60.31	49.71	48.66	63.97	52.99	6.28	106	13
α -CHLORDAN	50	50.15	44.57	53.97	55.77	47.04	58.65	49.56	47.51	61.87	52.12	5.80	104	12
DIELDRIN	50	50.89	48.71	56.93	59.97	50.36	60.12	52.99	48.72	62.39	54.56	5.35	109	11
op' -DDT	125	123.70	102.82	125.92	133.04	117.08	146.43	114.13	119.84	149.68	125.85	15.12	101	12
THIODAN-2	100	102.37	99.71	115.07	122.31	102.80	118.06	107.73	102.36	119.47	109.99	8.74	110	9
MIREX	125	127.53	98.32	113.74	125.17	127.03	147.51	105.84	125.25	139.29	123.30	15.42	99	12
METHOXY	125	126.93	113.73	137.12	147.32	122.57	143.34	124.03	121.09	138.41	130.50	11.41	104	9
135-TBB (surrogate)	125	132.06	133.55	155.18	163.79	130.99	155.99	144.52	127.38	166.95	145.60	15.25	116	12

July 7, 1994: Comparison of methods.
 Recovery of OC/CB "A" compounds spiked into Verner raw water. Method OWOC-E3120B.
 Quantitation by internal standard.

Compound	Spiking conc., (ng/L)	Recovery (ng/L)									ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8	9				
HCE	25	22.82	23.34	23.34	23.02	22.84	23.41	24.43	23.58	23.58	23.19	0.68	93	3
124-TCB	125	118.75	121.78	116.35	116.46	115.08	117.01	116.67	120.34	120.34	117.36	2.52	94	2
123-TCB	125	124.98	126.35	125.04	123.99	123.42	125.16	124.99	125.65	125.65	124.92	0.85	100	1
236-TCT	125	115.37	118.66	118.42	119.47	115.83	114.16	116.90	114.32	114.32	116.45	1.99	93	2
1235-TCB	25	24.40	24.75	25.09	25.22	24.34	23.82	24.29	24.06	24.06	24.32	0.70	97	3
26 α -TCT	125	131.05	129.11	128.68	130.18	130.40	133.46	129.31	132.01	132.01	130.84	1.77	105	1
PENTA	25	25.09	24.85	24.82	24.95	24.90	24.68	24.73	24.76	24.76	24.83	0.14	99	1
TRIFLURALIN	125	110.79	100.00	103.32	100.68	103.08	111.92	104.92	111.36	111.36	107.44	6.81	86	5
α -BHC	25	21.95	21.41	21.35	21.27	21.86	22.04	21.39	21.57	21.57	21.73	0.48	87	2
HEPTACHLOR	25	22.63	21.44	21.64	21.30	22.92	22.47	21.38	22.42	22.42	22.18	0.77	89	3
OXYCHLOR	50	46.55	42.44	43.05	42.93	44.62	45.99	42.60	46.19	46.19	44.58	1.84	89	4
γ -CHLORDAN	50	47.33	41.76	42.98	42.92	44.92	47.75	42.48	47.20	47.20	44.97	2.47	90	5
α -CHLORDAN	50	46.83	41.18	42.87	42.02	44.30	46.37	42.28	46.00	46.00	44.19	2.15	88	4
DIELDRIN	50	47.26	44.74	44.96	44.92	47.11	47.23	44.95	46.90	46.90	46.00	1.12	92	2
op' -DDT	125	114.91	94.47	99.53	99.69	109.64	115.12	96.87	115.41	115.41	106.20	8.51	85	7
THIODAN-2	100	95.09	91.60	90.93	91.64	96.24	92.82	91.44	98.50	98.50	92.90	3.17	93	3
MIREX	125	118.77	90.53	90.08	93.95	119.21	116.22	90.05	120.96	120.96	104.74	13.94	84	11
METHOXY	125	115.09	101.96	105.74	107.59	112.01	109.98	102.75	113.88	113.88	107.60	5.55	86	4

July 7, 1994: Comparison of methods.
 Recovery of OC/CB "A" compounds spiked into Verner raw water. Hexane micro-extraction.
 Quantitation by external standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
HCE	25	24.14	23.13	22.42	24.73	26.33	22.27	24.83	20.35	23.53	1.87	94	7
124-TCB	125	125.61	115.16	114.36	110.36	112.78	125.19	106.36	100.82	113.83	8.52	91	7
123-TCB	125	123.51	115.29	113.97	111.36	113.85	114.87	108.58	103.73	113.14	5.72	91	5
236-TCT	125	124.37	119.81	117.00	114.57	124.10	136.27	109.97	107.76	119.23	9.14	95	7
1235-TCB	25	24.80	23.78	24.09	22.80	24.33	22.69	22.29	21.32	23.26	1.18	93	5
26 α -TCT	125	120.55	113.54	110.17	106.77	114.79	116.51	103.94	100.91	110.90	6.68	89	5
PENTA	25	22.39	21.98	21.21	21.40	26.15	28.82	21.08	21.61	23.08	2.84	92	11
TRIFLURALIN	125	119.38	120.95	112.17	106.94	138.01	123.34	108.28	103.82	116.61	11.19	93	9
α -BHC	25	18.36	17.92	16.78	16.20	17.48	17.64	15.79	15.43	16.95	1.06	68	4
HEPTACHLOR	25	22.47	22.59	20.63	19.59	23.23	21.10	19.84	18.99	21.06	1.56	94	6
OXYCHLOR	50	44.70	44.13	41.50	39.20	39.73	37.10	38.87	35.73	40.12	3.16	80	6
γ -CHLORDAN	50	45.05	44.20	41.39	38.82	40.55	37.59	39.17	36.42	40.40	3.04	81	6
α -CHLORDAN	50	44.93	44.36	40.98	38.41	40.29	37.29	38.45	35.97	40.08	3.22	80	6
DIELDRIN	50	48.40	45.68	44.42	42.06	45.58	42.94	40.88	38.74	43.59	3.07	87	6
op'-DDT	125	110.26	108.66	99.16	92.01	96.75	90.55	92.74	87.18	97.16	8.43	78	7
THIODAN-2	100	101.12	91.94	91.06	86.30	87.10	90.38	84.19	82.88	89.37	5.76	89	6
MIREX	125	97.25	102.38	86.52	79.30	81.22	82.93	79.96	82.76	86.54	8.59	69	7
METHOXY	125	124.00	117.13	112.16	105.79	107.56	105.06	103.28	99.90	109.36	7.96	87	6
135-TBB (surrogate)	125	124.19	117.53	115.27	112.48	120.90	121.12	110.33	106.38	116.03	6.06	93	5

July 7, 1994: Comparison of methods.
 Recovery of OC/CB "A" compounds spiked into Verner raw water. Hexane micro-extraction.
 Quantitation by internal standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
HCE	25	22.77	23.04	22.76	25.53	25.24	21.50	26.20	22.35	23.67	1.72	95	7
124-TCB	125	124.50	120.57	122.09	120.73	114.78	127.08	118.65	116.62	120.63	4.02	96	3
123-TCB	125	122.97	121.25	122.24	122.40	116.49	117.28	121.64	120.48	120.59	2.42	96	2
236-TCT	125	124.36	126.56	126.00	126.42	127.34	113.05	123.93	125.93	124.20	4.64	99	4
1235-TCB	25	24.57	24.88	25.72	24.94	24.78	23.05	24.81	24.63	24.67	0.75	99	3
260-TCT	125	120.32	119.70	118.44	117.64	117.67	119.26	116.80	117.62	118.43	1.22	95	1
PENTA	25	23.27	24.19	23.77	24.60	22.39	20.89	24.72	26.36	23.77	1.64	95	7
TRIFLURALIN	125	118.79	127.19	120.23	117.45	117.52	125.97	121.38	120.77	121.16	3.65	97	3
α -BHC	25	18.12	18.69	17.85	17.66	17.73	17.86	17.54	17.76	17.90	0.36	72	1
HEPTACHLOR	25	21.96	23.33	21.73	21.15	23.42	21.21	21.80	21.67	22.03	0.87	88	4
OXYCHLOR	50	44.11	46.01	44.13	42.72	40.31	37.55	43.17	41.15	42.39	2.65	85	5
γ -CHLORDAN	50	44.46	46.11	44.00	42.32	41.13	38.05	43.51	41.95	42.69	2.45	85	5
α -CHLORDAN	50	44.34	46.19	43.56	41.86	40.87	37.74	42.69	41.42	42.33	2.53	85	5
DIELDRIN	50	47.51	47.37	46.98	45.59	45.96	43.21	45.15	44.38	45.77	1.51	92	3
op' -DDT	125	108.23	112.69	104.87	99.75	97.61	91.16	102.22	99.87	102.05	6.63	82	5
THIODAN-2	100	97.58	93.75	94.67	91.96	86.37	89.44	91.44	93.35	92.32	3.40	92	3
MIREX	125	96.51	107.36	92.51	86.90	82.85	84.40	89.22	95.85	91.95	7.99	74	6
METHOXY	125	120.07	119.84	117.02	113.14	107.07	104.35	112.53	112.89	113.36	5.63	91	4

June 14, 1994: Comparison of methods.
 Recovery of OC/CB "B" compounds spiked into Verner raw water. Method OMOC-E3120B.
 Quantitation by internal standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
135-TCB	125	104.82	103.11	105.85	103.96	112.08	109.17	111.78	109.79	107.57	3.57	86	3
HCBD	25	15.90	16.94	16.20	17.27	17.12	17.21	17.44	16.51	16.82	0.56	67	2
245-TCT	125	120.78	122.36	126.49	123.61	130.22	126.87	129.65	133.83	126.73	4.40	101	4
1245-TCB	25	25.23	24.39	28.90	26.57	27.20	25.57	26.99	29.78	26.83	1.83	107	7
CYCLOPENT	50	29.87	19.90	29.04	32.84	18.41	19.56	24.92	37.93	26.56	7.05	53	28
1234-TCB	25	26.97	26.22	27.33	27.38	26.75	28.55	28.72	28.80	27.59	0.98	110	1
HCB	25	23.61	24.48	23.81	24.06	23.67	24.36	24.24	24.01	24.03	0.32	96	1
LINDANE	25	26.06	26.69	26.77	26.75	26.20	26.72	26.44	26.45	26.51	0.27	106	1
ALDRIN	25	21.35	20.95	21.47	20.66	20.64	21.59	21.30	21.22	21.15	0.36	85	1
HEPTOXIDE	25	25.08	25.59	25.28	25.72	24.98	25.65	25.50	25.19	25.37	0.28	101	1
OCTA	25	19.60	19.23	20.76	17.00	18.38	19.52	19.18	19.1	19.35	0.68	77	3
THIODAN-1	50	48.16	48.70	48.69	49.19	47.99	48.97	48.37	48.4	48.57	0.40	97	1
pp'-DDE	125	102.05	102.04	108.33	101.33	93.81	100.25	98.13	97.74	100.46	4.22	80	3
ENDRIN	100	106.47	106.91	108.12	109.21	106.40	109.79	108.63	109.85	108.17	1.43	108	1
pp'-DDD	125	117.13	117.12	118.54	118.46	113.50	119.11	116.80	116.04	117.09	1.78	94	1
THIO-SS	100	96.03	96.71	96.91	98.29	95.61	98.96	97.31	98.42	97.28	1.19	97	1
pp'-DDT	125	108.44	108.52	115.84	106.81	96.59	107.12	104.49	105.13	106.62	5.34	85	4

June 14, 1994: Comparison of methods.
Recovery of OC/CB "B" compounds spiked into Verner raw water. Hexane micro-extraction.
Quantitation by internal standard.

Compound	Spiking conc. (ng/L)	Recovery (ng/L)								ave. rec. (ng/L)	std. dev. (ng/L)	ave. % rec.	std. dev. (%)
		1	2	3	4	5	6	7	8				
135-TCB	125	116.80	120.03	121.66	122.16	118.07	126.41	121.48	126.60	121.65	3.51	97	3
HCBD	25	20.32	22.62	21.02	20.24	21.53	21.59	21.03	21.19	21.19	0.76	85	3
245-TCT	125	119.27	122.97	122.65	119.70	120.29	121.86	122.45	120.22	121.18	1.46	97	1
1245-TCB	25	24.19	25.36	27.02	25.19	25.80	25.42	25.62	24.92	25.44	0.81	102	3
CYCLOPENT	50	32.73	37.77	35.73	31.48	36.65	38.38	34.42	36.87	35.50	2.44	71	5
1234-TCB	25	25.55	25.24	24.84	24.92	26.40	24.75	25.41	25.16	25.28	0.53	101	2
HCB	25	24.71	27.54	24.54	26.45	25.00	25.34	25.74	25.64	25.62	0.99	102	4
LINDANE	25	21.44	20.55	20.40	20.73	20.24	20.83	21.27	21.26	20.84	0.44	83	2
ALDRIN	25	22.77	22.31	22.00	21.86	22.03	23.11	22.32	23.13	22.44	0.50	90	2
HEPTOXIDE	25	24.66	24.45	23.80	24.24	24.42	24.55	24.29	25.38	24.47	0.45	98	2
OCTA	25	22.07	21.94	21.55	21.45	21.29	22.83	21.96	22.24	21.92	0.49	88	2
THIODAN-1	50	49.34	49.10	47.92	48.77	49.46	49.05	48.78	51.01	49.18	0.88	98	2
pp'-DDE	125	112.23	111.24	110.04	112.03	111.90	116.96	112.69	117.23	113.04	2.62	90	2
ENDRIN	100	108.06	108.14	104.79	108.34	107.16	108.75	106.63	113.50	108.17	2.50	108	2
pp'-DDD	125	120.95	121.93	119.41	122.26	122.94	125.63	105.37	130.05	121.07	7.13	97	6
THIO-SS	100	90.58	89.91	89.28	93.06	92.87	93.27	90.67	97.19	92.10	2.56	92	3
pp'-DDT	125	120.76	115.88	113.26	115.95	116.67	120.58	116.72	123.70	117.94	3.41	94	3

APPENDIX 4:

INTERPRETATION OF DATA FROM A STUDY INVESTIGATING THE STABILITY OF TRIFLURALIN IN SOLUTION

A4.1. Background and results of Trifluralin study

Throughout this work, it was observed that aging of the spiking and calibration standards corresponded with substantial over-recovery of Trifluralin. Similar trends were also seen for this compound during the routine activities using method OWOC-E3120 and as a result, an independent study was conducted from June to November, 1994 to investigate the stability of Trifluralin in hexane, sample extracts and water.

To rule out the interaction of Trifluralin with other compounds contained in OC/CB "A" solutions, standards containing only Trifluralin were used. Quantitative results were based on external standard calculations. The calibration standard used was the same one used for routine analyses, which was prepared in isooctane. The results did not indicate any particular trends over time. A possible source of confusion from this study was that these results were derived from external standard calculations.

Figure A4-1 shows that the peak areas for all samples (D607, D608, 50-S, 50-E, 100-S and 100-E) were variable from one analysis to another, yet no significant net change as a function of time was indicated. However, this data might have been misinterpreted, since there was no information on instrumental changes (detector response and injection volumes) over the same time frames. Control experiments, using other compounds known to be stable in these types of solutions, should have been conducted to give an indication of variabilities associated with instrument performance.

For example, Figure A4-2 shows the average detector response versus time for three different compounds, based on the injections of the calibration standard. This shows that while Trifluralin area counts did not significantly change over time, those of 1,3,5-Tribromobenzene and α -BHC steadily

increased. These two particular compounds were chosen to contrast the Trifluralin results because α -BHC is an adjacent peak to Trifluralin in the chromatographic analysis, and 1,3,5-Tribromo-benzene was used as the internal standard for the hexane micro-extraction work. These results imply that in comparison with these other two compounds, Trifluralin is not stable in the calibration standard.

This is more clearly shown by comparing ratios of the peak areas of these compounds to that of the internal standard, as presented in Figures A4-3. This indicates that, with the exception of one outlying point, the ratio of peak areas relative to 1,3,5-Tribromobenzene remains stable for α -BHC, while it ultimately drops off with Trifluralin. Figure A4-4 presents this concept a little differently, in that all values plotted were calculated as percentages of the initial points. This normalizes all values to the same scale, independent of the magnitude of the peak areas and ratios. A chlorinated analog of the internal standard is also presented as a contrast to the α -BHC data. This shows a definite decrease over time for Trifluralin in the calibration standard, while the relative responses of the other two compounds randomly fluctuate.

A4.2. Significance and recommendations

The results as interpreted here implies that Trifluralin was not stable in the calibration standard made up with isooctane. The stability of Trifluralin in isooctane was previously established during a one year period in 1993 (Ram Sadana, personal communication, January 27, 1995), therefore this may be due to reactions with other compound(s). If the kinetics of the process is slower in acetone, this would explain the apparent over-recoveries observed for Trifluralin as both the spiking and calibration standards aged. Throughout the work related to hexane micro-extraction, all calibra-

tion files were up-dated with each GC injection of calibration standard, thereby lowering the value of the relative response factor for this compound, and artificially increasing the recovery from the (more preserved) spiked sample extract. Notably, this assumes that whatever reaction affects Trifluralin in isooctane, also occurs in hexane.

To confirm these results it is recommended that another more extensive study be conducted, comparing detector responses over time (relative to the internal standard) for all OC/CB "A" compounds dissolved in hexane, isooctane and acetone, with and without the presence of Trifluralin. A minimum of triplicate analyses should be conducted for each solution at each time point. If Trifluralin degradation is due to reaction with another component of the mixture, deviations between the experiment and control should give an indication to which compounds react. Concurrently, more information on the effect of solvent type can be obtained.

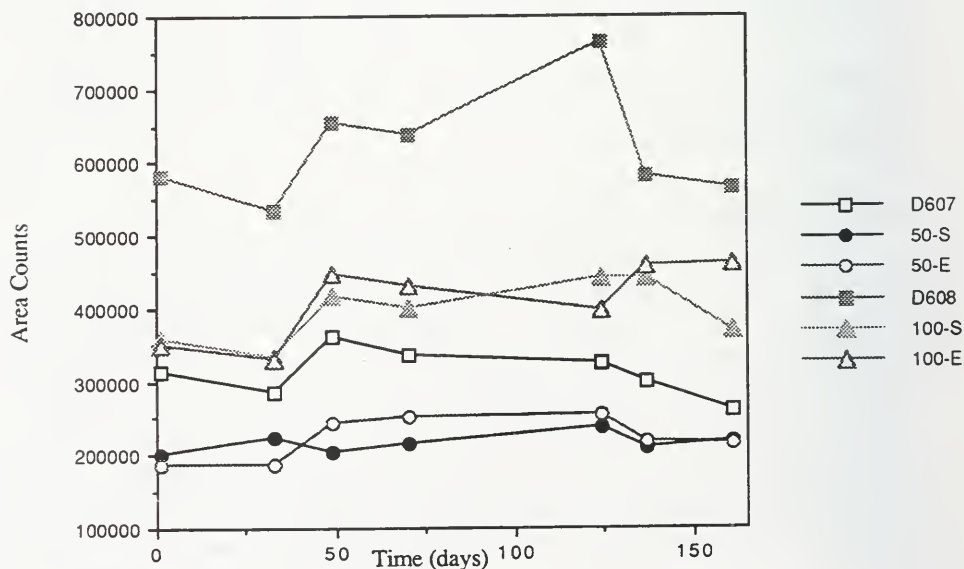


Figure A4-1: Trifluralin area counts versus time

Examples of area counts versus time for compounds in the instrument calibration standard

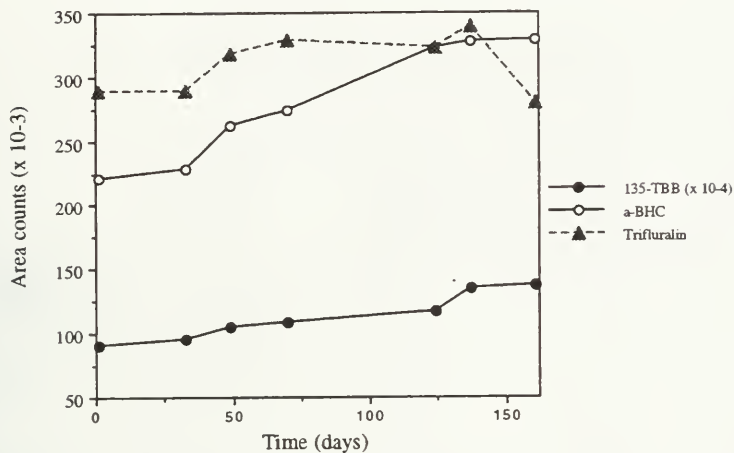


Figure A4-2: Area counts versus time for three compounds; from analysis of calibration standard.

Examples of area counts relative to 135-TBB

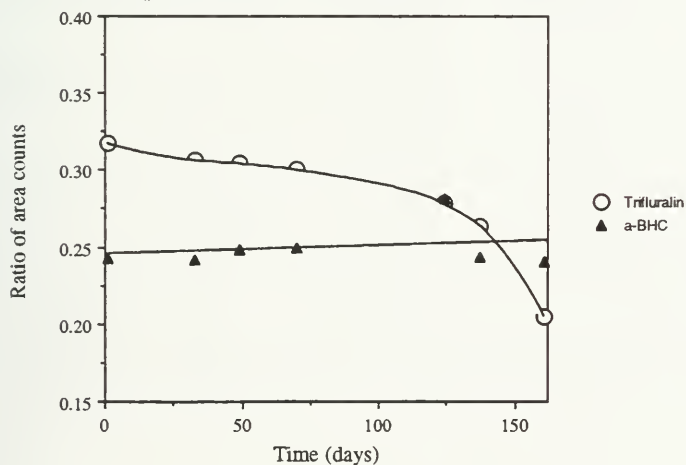


Figure A4-3: Ratios of analyte peak areas to 1,3,5-Tribromo benzene peak areas

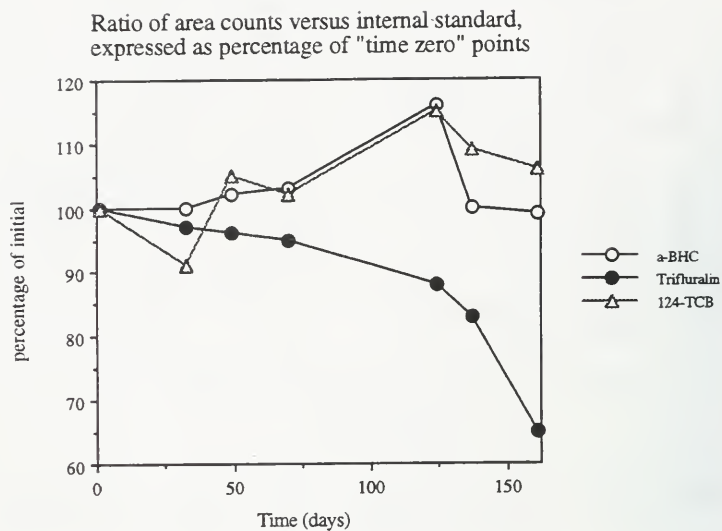


Figure A4-4: Peak area ratios versus time, expressed as percentage of original values

Table A4-1: Raw data from calibration standard used.

Date and run ID ^A		Area counts (average of both channels)			
		135-TBB	124-TCB ^B	α -BHC	Trifluralin
16/6/94	1	898315	111176	217073	288802
	2	903904	113539	223831	294020
	3	930893	113239	221241	283060
19/7/94	1	1146900	143124	264305	311258
	2	896152	116742	216554	269696
	3	856343	104369	213947	268116
	E	896453	107614	219322	285928
4/8/94	1	1093972	132969	271553	326880
	2	1037540	130707	262591	314004
	3	1019157	127743	254122	307056
	E	1036671	131317	256235	325929
25/8/94	1	1104543	137739	274514	323708
	2	1213636	150988	304161	360998
	3	1139428	143795	287147	337665
	E	918432	119621	227472	290228
18/10/94	1	1359379	180029	355720	362652
	2	1106092	159179	297102	307888
	3	1142270	155894	365568	318274
	E	1057490	148101	290112	301731
31/10/94	1	1825148	240960	441080	300636
	2	1190573	160425	286510	445087
	3	1220678	163471	294894	299328
	E	1141735	166012	284140	309354
24/11/94	1	1313526	173260	318018	268475
	2	1545595	194723	357140	301738
	E	1242772	171651	311391	269706

A: E denotes last run in sequence

B: Channel 2 only; accuracy of channel 1 areas for this compound were suspected to be inaccurate (Ram Sadana, Personal communication, January 27, 1995)

Table A4-2: Average ratios of areas counts^A
(standard deviations in parentheses)

Date:	124-TCB ^B	α -BHC	Trifluralin
16/6/94	0.136 (0.007)	0.243 (0.005)	0.317 (0.011)
19/7/94	0.124 (0.006)	0.242 (0.008)	0.316 (0.013)
4/8/94	0.143 (0.003)	0.249 (0.003)	0.304 (0.007)
25/8/94	0.139 (0.004)	0.250 (0.002)	0.300 (0.010)
18/10/94	0.157 (0.005)	0.281 (0.026)	0.278 (0.007)
31/10/94	0.148 (0.009)	0.244 (0.004)	0.264 (0.086)
24/11/94	0.144 (0.006)	0.241 (0.010)	0.205 (0.011)

A: Selected compound - to- 1,3,5-Tribromobenzene
Ratios calculated for each run, then averaged.

B: Calculated from channel 2 data only.

Table A4-3: Ratios as percentage of initial time point

Date:	124-TCB ^B	α -BHC	Trifluralin
16/6/94	100	100	100
19/7/94	91	100	100
4/8/94	105	102	96
25/8/94	102	103	95
18/10/94	115	116	88
31/10/94	109	100	83
24/11/94	106	99	65

